



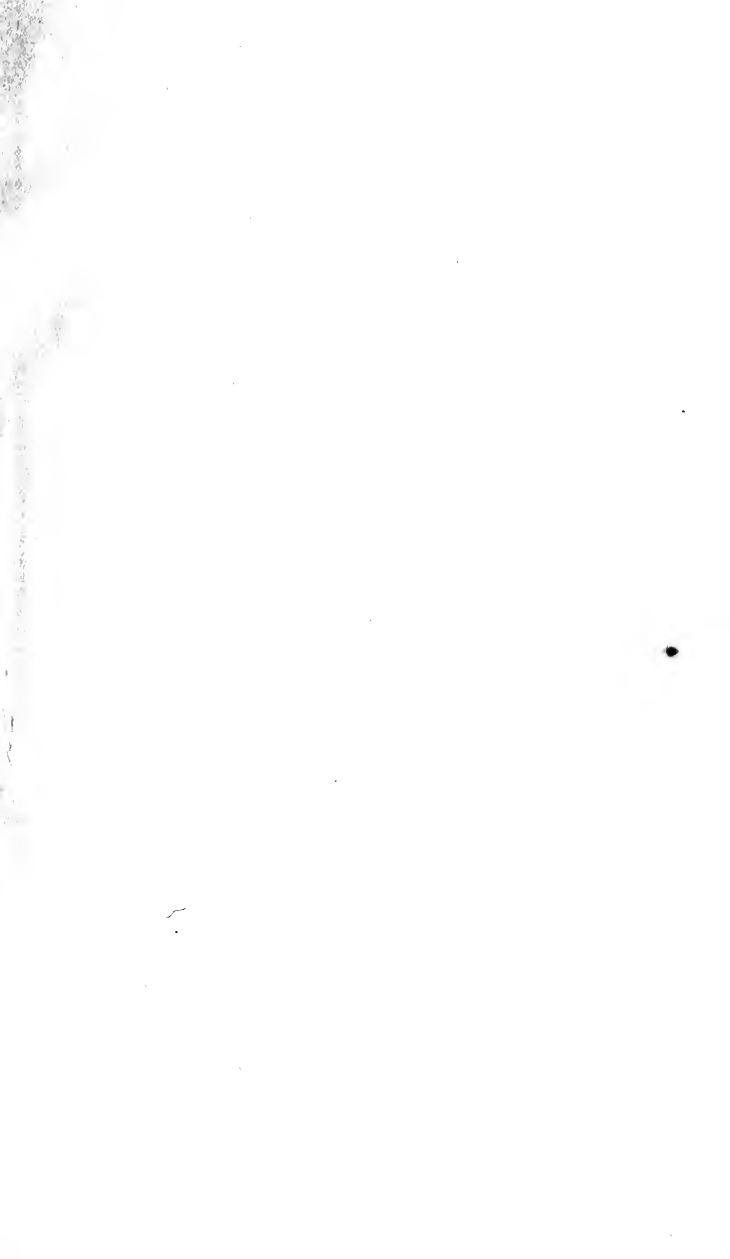


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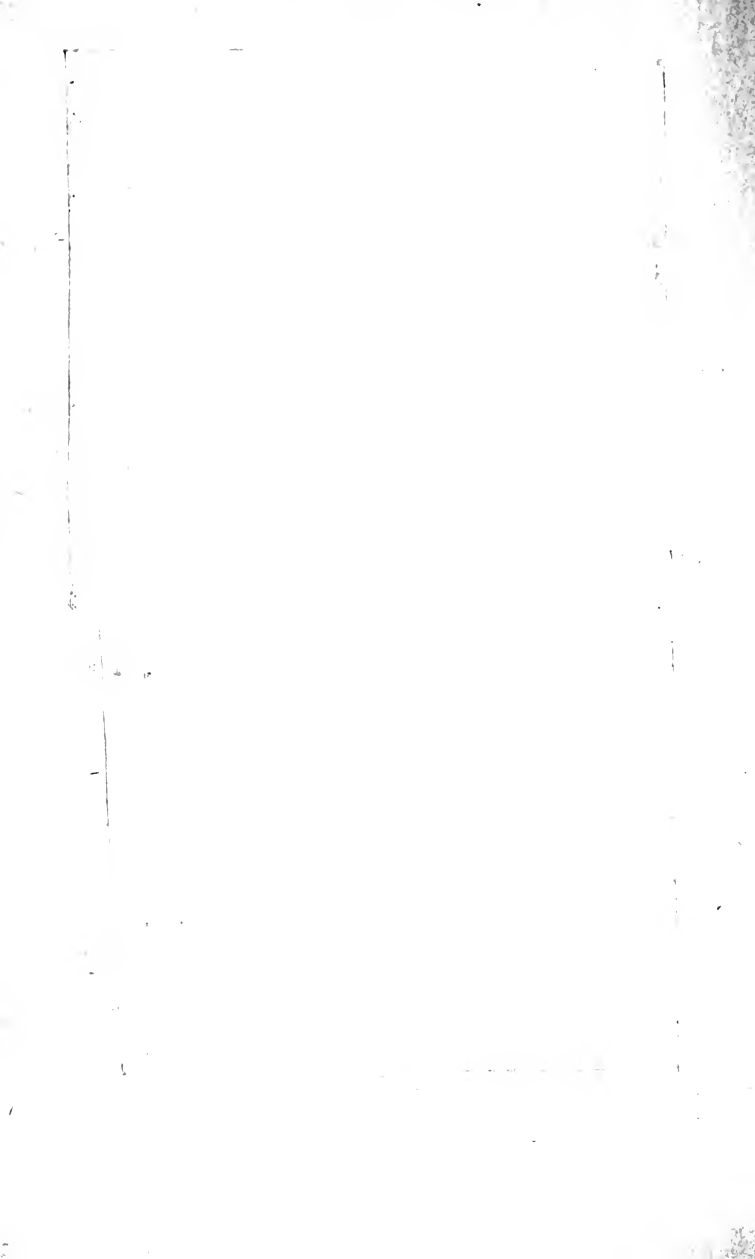
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AMERICAN CHEMICAL JOURNAL.

Contributions from the Chemical Laboratory of Harvard College.

LXV.—ON SOME NITRO DERIVATIVES OF METABROMTOLUOL.

BY W. B. BENTLEY AND W. H. WARREN.¹

Determination of the Constitution of Metabromdinitrotoluol, $C_6H_2CH_3Br(NO_2)_2$.

Our attention was first called to this subject by Prof. C. Loring Jackson, who, having with W. S. Robinson² obtained the metabromdinitrotoluol by the decomposition of their bromdinitrophenylmalonic ester, asked us to determine its constitution.

This metabromdinitrotoluol, melting point 103° – 104° , was discovered by Grete,³ who made it by the action of fuming nitric acid on metabromtoluol, or metabrommonitrotoluol, and assigned to it the constitution CH_3 , NO_2 , Br , NO_2 , 1, 2, 3, 4, although he was very doubtful about the position of the second nitro group, giving it the para position without any experimental reason for doing so. His proof that one of the nitro groups was in the ortho position consisted in establishing the identity of the bromtoluidine made by the reduction of his bromnitrotoluol with that obtained by the action of bromine on orthoacetoluid;⁴ but this obviously leaves it

¹ Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

² This Journal 11.

³ Ann. Chem. (Liebig) 168, 258.

⁴ Wroblewsky, Ann. Chem. (Liebig) 168, 161.

doubtful whether this nitro group stands in the position 2 or 6 to the methyl of the toluol, and in fact later work has shown that Grete was wrong in ascribing to it the position 2, as his mononitro compound really has the constitution $\text{CH}_3, \text{Br}, \text{NO}_2, 1, 3, 6$. The proof of this was given by Nevile and Winther,¹ who, by replacing the amido group in the metabromorthotoluidine (melting point $55^\circ\text{--}56^\circ$) already mentioned by bromine, obtained a liquid dibrom-toluol, which on oxidation with nitric acid yielded the dibrombenzoic acid melting at $151^\circ\text{--}153^\circ$ previously made by Von Richter² from paradibrombenzol.

The only point therefore not settled in regard to the constitution of Grete's metabromdinitrotoluol was the position of the second nitro group, which might be either para or ortho to the methyl. To determine this the metabromdinitrotoluol was heated with alcoholic ammonia³ in sealed tubes to 100° for twelve hours, when it was found to be converted into a yellow substance, which had partly separated in the solid state, and partly remained in solution in the alcohol, from which it was obtained by evaporation. The product was purified by washing with water to remove the ammonic bromide, and crystallisation from hot glacial acetic acid, until it showed a constant melting point ($193^\circ\text{--}194^\circ$), when it was dried at 135° , and the following analysis showed that a dinitro-metatoluidine had been formed.

0.2658 gram of the substance gave 51.2 cc. of nitrogen at a temperature of 24° and a pressure of 767.5 mm.

	Calculated for $\text{C}_6\text{H}_2\text{CH}_3\text{NH}_2(\text{NO}_2)_2$.	Found.
Nitrogen	21.31	21.71

The melting point showed that this substance is identical with the dinitrotoluidine made by Hepp⁴ by the action of alcoholic ammonia on his γ trinitrotoluol, but the constitution of this trinitrotoluol had not been determined. Staedel⁵ has also announced recently that one of his students, Herr Adalbert Kolb, has prepared a dinitrotoluidine from dinitrokresolether and determined its constitution as $\text{CH}_3, \text{NH}_2, \text{NO}_2, \text{NO}_2, 1, 3, 4, 6$; but, as he neglected to give the melting point, we were unable to tell whether it was identical with ours or not, and have been forced to work

¹ Ber. d. chem. Gesell. **13**, 962.

² Ibid. **7**, 1146.

³ When metabromdinitrotoluol was allowed to stand with alcoholic ammonia in the cold, a dark blue solution was formed at first, but the color gradually changed to reddish brown.

⁴ Ann. Chem. (Liebig) **215**, 371.

⁵ Ber. d. chem. Gesell. **22**, 215.

out the constitution of our dinitrotoluidine by the replacement of the amido group by hydrogen. In doing this some difficulty was encountered because of the very slight solubility of the dinitrotoluidine in alcohol, but we found on experiment that the Griess reaction would take place satisfactorily in a mixture of acetone and alcohol, and accordingly proceeded as follows: 2 grams of the dinitrotoluidine were dissolved in about 12 cc. of acetone, 8 cc. of common alcohol added, and the mixture acidified with strong sulphuric acid, after which 1.5 grams of sodic nitrite, about twice the calculated amount, was added in small portions at a time, and the liquid warmed gently until the evolution of nitrogen ceased, when the larger part of the acetone and alcohol was distilled off at first on the water-bath, finally on the sand-bath, and the residue distilled with steam; the dinitrotoluol passed over into the receiver in small white crystals, which were removed by filtration, and crystallised from hot alcohol until they showed the constant melting point 71° . It was not worth while to dilute the distillate of acetone and alcohol, as no precipitate was obtained in that way. For greater certainty the product was analysed, with the following results:

0.2456 gram of the substance gave 33.1 cc. of nitrogen at a temperature of 22° and a pressure of 764.2 mm.

	Calculated for $C_6H_3CH_3(NO_2)_2$.	Found.
Nitrogen	15.38	15.29

There is no question, therefore, that the substance is the ortho-paradinitrotoluol, CH_3 , NO_2 , NO_2 , 1, 2, 4, and the bromdinitrotoluol accordingly has the following constitution: CH_3 , Br, NO_2 , NO_2 , 1, 3, 4, 6. It follows also that our dinitrotoluidine is identical with that described by Kolb, and, if Staedel had given its melting point, it would not have been necessary for us to determine its constitution. As has been already stated, this dinitrotoluidine melts at the same point as that made by Hepp from alcoholic ammonia and his γ trinitrotoluol. To establish the relation between these substances more firmly, we made the dinitrophenyltoluidine by treating our dinitrobromtoluol with aniline, and found that the product showed the same melting point, 142° , as that of the compound made by Hepp from γ trinitrotoluol and aniline. The γ trinitrotoluol of Hepp, therefore, has the following constitution: CH_3 , NO_2 , NO_2 , NO_2 , 1, 3, 4, 6; which is in harmony

with Laubenheimer's rule,¹ that a nitro group is removed by the action of alcoholic ammonia only when it is in the ortho position to another nitro group.

Metabromtrinitrotoluol, $C_6HCH_3Br(NO_2)_3$.

In preparing the metabromdinitrotoluol we found, if a mixture of fuming nitric acid and sulphuric acid was used, that a new substance melting above 104° was obtained, which turned out to be the as yet undescribed metabromtrinitrotoluol. This compound is most easily prepared from the metabromdinitrotoluol, when it is convenient to proceed as follows: 5 to 10 grams of metabromdinitrotoluol were placed in a flask, and 10 to 20 cc. of a mixture of two volumes of fuming nitric acid and one of strong sulphuric acid added. The whole was then boiled until the evolution of red fumes had nearly ceased, when, after it was cool, it was poured in a fine stream into a beaker of cold water, stirring the liquid vigorously during the addition of the acid solution, as in this way the product is precipitated in a granular form much more easy to manage than the large compact lumps obtained if the stirring is neglected. The product was then washed with cold water till free from acid, and purified by crystallisation from alcohol, until it showed the constant melting point 143° . The residue from the mother liquors, consisting of a mixture of metabromtrinitrotoluol and the corresponding dinitro compound, can be advantageously used for preparing a fresh quantity of the trinitro body. The pure substance was dried at 120° , and analysed with the following results:

I. 0.3372 gram of the substance gave on combustion 0.3356 gram of carbonic dioxide and 0.0453 gram of water.

II. 0.2651 gram of the substance gave 32.9 cc. of nitrogen at a temperature of 21° and a pressure of 761.5 mm.

III. 0.1830 gram of the substance gave, by the method of Carius, 0.1120 gram of argentic bromide.

	Calculated for $C_6HCH_3Br(NO_2)_3$.	I:	Found. II.	III.
Carbon	27.46	27.14
Hydrogen	1.31	1.49
Nitrogen	26.14	...	26.04	...
Bromine	13.73	14.09

The yield was about 60 per cent. of the theoretical.

¹ Ber. d. chem. Gesell. 9, 766, 1828.

Properties.—The metabromtrinitrotoluol crystallises from alcohol in small white needles, which melt at 143° . They are insoluble in water or ligroin; nearly insoluble in cold alcohol, only sparingly soluble in hot; slightly soluble in carbonic disulphide; soluble in ether, methyl alcohol, benzol, chloroform, glacial acetic acid, or acetone. Boiling alcohol we found the best solvent for it, although it is so slightly soluble in it. Aqueous sodic hydrate seemed to have no action upon it, nor was it affected by the strong acids. The bromine is removed easily, which we proved by the action of alcoholic ammonia or aniline on it, as will be described later in this paper.

Constitution of Metabromtrinitrotoluol.

As the metabromtrinitrotoluol is made from the metabromdinitrotoluol, the only point to be determined is the position of the third nitro group; for this purpose we converted it into the corresponding trinitrotoluidine by treatment with alcoholic ammonia in the cold. The mixture was allowed to stand in a corked flask for about twelve hours; at first a dark blue color appeared in the liquid, but on longer standing this turned to a deep reddish brown, and a precipitate was deposited, which with the supernatant liquid at the end of the twelve hours was poured into a dish and the solvent allowed to evaporate spontaneously. The residue, which was red and yellow, was washed till free from ammonic bromide, and then purified by crystallisation from hot glacial acetic acid, until it showed the constant melting point 136° , when it was dried at 120° and analysed with the following result:

0.1144 gram of the substance gave 24.2 cc. of nitrogen at a temperature of 23° and a pressure of 754.7 mm.

Nitrogen	Calculated for	Found.
	$C_6HCH_3NH_2(NO_2)_3$.	
	23.14	23.51

The melting point of this trinitrotoluidine shows that it is identical with that prepared by Nölting and Salis¹ by the action of alcoholic ammonia on trinitrometakresolethylether, to which they assign the constitution CH_3 , NO_2 , NH_2 , NO_2 , NO_2 , 1, 2, 3, 4, 6, on the ground that the alcoholic ammonia did not remove any of the nitro groups, and therefore, according to Laubenheimer,² no two of them could be in the ortho position to each other, and this is the only possible arrangement in which no two nitro groups are

¹ Ber. d. chem. Gesell. 15, 1864.

² Ibid. 9, 766, 1828.

in the ortho position. Our metabromtrinitrotoluol must consequently have the constitution $\text{CH}_3, \text{NO}_2, \text{Br}, \text{NO}_2, \text{NO}_2, 1, 2, 3, 4, 6$; and this conclusion is confirmed by the fact recently discovered in this laboratory,¹ that the bromtrinitrophenylmalonic ester is converted by boiling with sulphuric acid of specific gravity 1.44 into this metabromtrinitrotoluol melting at 143° . As the bromtrinitrophenylmalonic ester is made from the symmetrical tribromtrinitrobenzol, $\text{Br}, \text{NO}_2, \text{Br}, \text{NO}_2, \text{Br}, \text{NO}_2, 1, 2, 3, 4, 5, 6$, it can have only the constitution $\text{CH}(\text{COOC}_2\text{H}_5)_2, \text{NO}_2, \text{Br}, \text{NO}_2, \text{NO}_2, 1, 2, 3, 4, 6$, which leads to the constitution of our metabromtrinitrotoluol given above.

Anilidotrinitrotoluol, $\text{C}_6\text{HCH}_2(\text{C}_6\text{H}_5\text{NH})(\text{NO}_2)_3$.

This substance was prepared by treating metabromtrinitrotoluol with aniline in the proportion of two molecules of the base to one of the nitro compound; the action is violent, accompanied with considerable evolution of heat, and the product was easily purified by crystallisation from a mixture of alcohol and benzol, until it showed the constant melting point 151° , when it was dried at 120° , and analysed with the following results:

I. 0.2804 gram of the substance gave on combustion 0.5031 gram of carbonic dioxide and 0.0936 gram of water.

II. 0.2777 gram of the substance gave 43.2 cc. of nitrogen at a temperature of 27.5° and a pressure of 772 mm.

	Calculated for $\text{C}_6\text{HCH}_2(\text{C}_6\text{H}_5\text{NH})(\text{NO}_2)_3$.	I.	Found.	II.
Carbon	49.06	49.03
Hydrogen	3.14	3.71
Nitrogen	17.61	...	17.41	...

Properties.—The metanilidotrinitrotoluol crystallises from a mixture of alcohol and benzol in well developed shining yellow plates, which melt at 151° . The substance is insoluble in water or ligroin; sparingly soluble in ethyl or methyl alcohol; soluble in ether, chloroform, benzol, carbonic disulphide, glacial acetic acid, or acetone. The most convenient solvent for it is a mixture of five parts of alcohol with one of benzol. Aqueous sodic hydrate dissolves it with a red color, and hydrochloric acid throws down from this solution the original substance apparently unaltered.

¹ See next paper, page 19.

Strong sulphuric or strong nitric acid dissolves it, but strong hydrochloric acid does not.

The constitution of this substance is CH_3 , NO_2 , $\text{C}_6\text{H}_5\text{NH}$, NO_2 , NO_2 , 1, 2, 3, 4, 6, as is shown by its preparation from the meta-bromtrinitrotoluol, the constitution of which has been determined, as given earlier in this paper.

LXVI.—ON THE ACTION OF SODIUM MALONIC ESTER UPON TRIBROMTRINITROBENZOL.

BY C. LORING JACKSON AND GEORGE DUNNING MOORE.¹

In a previous paper² one of us with J. F. Wing described the preparation of tribromtrinitrobenzol, and announced that its action with sodium malonic ester would be studied. This work promised to be of especial interest, because we hoped that each of the bromine atoms would be replaced by the radical $\text{CH}(\text{COOC}_2\text{H}_5)_2$, and that by the reduction of the substance thus formed a compound might be obtained consisting of three pyrrol molecules united to form a central benzol ring, a sort of triple indol. Our first experiments, however, showed that the reaction did not run in the way we had expected, but instead of the removal of all three of the bromine atoms only two were replaced, one by the radical $\text{CH}(\text{COOC}_2\text{H}_5)_2$, the other by hydrogen giving a product with the following formula,



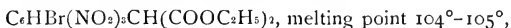
that is, bromtrinitrophenylmalonic ester. After we had established the composition of this substance, we decided that it was unwise to undertake a complete study of this trinitro compound, which can be obtained only with a very considerable outlay of time and material, when the corresponding dinitro compound can be made much more easily, and resembles it closely in most respects. We have accordingly confined our work principally to those properties of the trinitro compound in which we have observed marked differences from the corresponding ones of the dinitro body, and for a fuller discussion of those properties which the two substances

¹ Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

² This Journal 10, 283 (1888).

have in common would refer the reader to a paper "On the Action of Sodium Malonic Ester on Tribromdinitrobenzol" by one of us and W. S. Robinson.¹

The results described in this paper can be briefly stated as follows. Sodium malonic ester forms in the cold with tribromtrinitrobenzol bromtrinitrophenylmalonic ester,

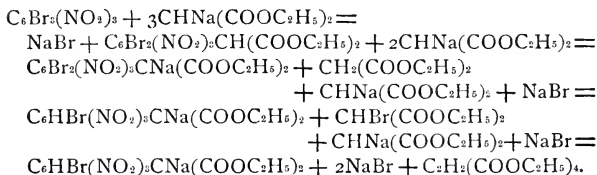


which has acid properties forming salts even with aqueous solutions of the alkaline carbonates. Of these the red soluble sodium salt has been studied, and its analysis led to the formula



The yellow insoluble copper salt, on the other hand, gave no constant result on analysis, but on several occasions, in trying to make it from a solution of cupric chloride in alcohol and the sodium salt, a crystalline substance free from copper was obtained melting in the neighborhood of 75° . Unfortunately the end of the term has prevented us from studying this substance, which is the more interesting because no similar compound has been obtained from the corresponding dinitro body.

The reactions by which the bromtrinitrophenylmalonic ester is derived from tribromtrinitrobenzol have been made out as follows:



The acetylentetracarboxylic ester formed according to the last reaction was obtained from the oily secondary product of the action by distillation under diminished pressure, and identified by its melting point and analysis.

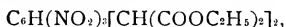
Perhaps the most striking difference between the dinitro and trinitro compounds consisted in the fact that the trinitro ester, or its salts, when heated with an excess of common strong nitric acid, turned bright blood-red, whereas no such action could be obtained from the dinitro compound. The red product, on crystallisation

¹ This Journal 11, 93 (1889).

from alcohol, was converted into colorless crystals melting at 215° , and as they melted becoming blood-red and increasing very much in volume. The study of this curious substance is still unfinished; we have only established the fact that it is an ester. If the action of the nitric acid is long continued, another body is formed melting at 156° to a colorless liquid, and dissolving in aqueous sodic hydrate with a red color.

Sulphuric acid of specific gravity 1.44 converts the ester into the metabromtrinitrotoluol melting at 143° – 144° , recently discovered in this laboratory by Bentley and Warren.

The trinitrophenylendimalonic ester (melting point 123°),



was also obtained by the further action of sodium malonic ester on bromtrinitrophenylmalonic ester; strangely enough, it has less marked acid properties than the bromine compound, from which it is derived.

Preparation of Bromtrinitrophenylmalonic Ester.

The tribromtrinitrobenzol used for this purpose was prepared according to the method already given by one of us and J. F. Wing;¹ we have found, however, that if the proportion of fuming sulphuric acid is increased, a better yield is obtained. The proportions finally used were 20 grams of tribromdinitrobenzol, 500 cc. of the nitric acid of 1.52 specific gravity, and 200 cc. of fuming sulphuric acid, instead of one-third the volume of the nitric acid as previously recommended. The yield obtained from the new proportions was in the neighborhood of 40 per cent. of the theory, running in one case as high as 45 per cent., whereas the proportions recommended by one of us and Wing gave on the average from 15 to 20 per cent., and only in a single instance ran as high as 40 per cent.

To convert the tribromtrinitrobenzol into bromtrinitrophenylmalonic ester, one molecule of it must be treated with about three molecules of sodium malonic ester. In practice we found it convenient to proceed as follows: 10 grams of tribromtrinitrobenzol were dissolved in about 100 cc. of benzol with the aid of heat, mixed, while the solution was still moderately warm, with 10.6 grams of malonic ester previously converted into the sodium com-

¹ This Journal 10, 284 (1888).

pound by treatment with the sodic ethylate from 1.7 grams of sodium (a slight excess over the calculated amount) and about 75 cc. of absolute alcohol, and the mixture allowed to stand 40 to 60 hours in a corked flask at ordinary temperatures. As soon as the sodium malonic ester was added the liquid became dark blood-red, and on standing this color gradually increased in intensity, while at the same time a precipitate of sodic bromide was thrown down. The product of the reaction was mixed with about three-quarters of a liter of water, and acidified with dilute sulphuric acid,¹ which decomposed the red salt, setting free the ester. Ether was then added, and, after shaking thoroughly, the ethereal and benzol solution separated from the aqueous liquid, which was extracted once more with ether. On distilling off the ether and benzol from the extract, a dark oily residue was left, which was mixed with a little alcohol, when, upon stirring, it solidified to a mass of prismatic crystals. These were sucked out on the pump, washed with a little cold alcohol to remove the adhering oil, and purified by crystallisation from hot alcohol, till they showed the constant melting point 104° – 105° . The oil which was sucked out from the crystals, or removed from them by alcohol, upon standing, deposited an additional amount of the substance, which was purified in the same way as the main portion. The substance, after being dried *in vacuo*, was analysed with the following results:

I. 0.2235 gram of the substance gave on combustion 0.2860 gram of carbonic dioxide and 0.0629 gram of water.

II. 0.1930 gram of the substance gave 16.2 cc. of nitrogen at a temperature of 21° and under a pressure of 775.9 mm.

III. 0.2548 gram gave 20.1 cc. of nitrogen at 18.5° and 784 mm. pressure.

IV. 0.2080 gram gave by the method of Carius 0.0870 gram of argentic bromide.

V. 0.2512 gram gave 0.1034 gram of argentic bromide.

	Calculated for $C_6HBr(NO_2)_3CH(COOC_2H_5)_2$.	I.	II.	Found. III.	IV.	V.
Carbon	34.67	34.89
Hydrogen	2.67	3.13
Nitrogen	9.33	...	9.75	9.38
Bromine	17.78	17.80	17.52

¹ Dilute nitric acid, which was used in some of the earlier preparations, seemed to diminish the yield.

The yield was good, when compared to that obtained in similar preparations from other substances; the best result was as follows: 10 grams of tribromtrinitrobenzol, treated as described above with 10.6 grams of malonic ester, gave 6.4 grams of bromtrinitrophenylmalonic ester. The amount required by theory, if all the tribromtrinitrobenzol had been converted into bromtrinitrophenylmalonic ester, is 10 grams; therefore the yield is 64 per cent. of the theoretical. The average yield was between 50 and 60 per cent. of the theoretical.

Properties.—The bromtrinitrophenylmalonic ester crystallises in white slender needles arranged in radiating groups, which, when examined with the microscope, are seen to be flat needles, or long plates terminated by one plane, or, as commonly, by two at an obtuse angle to each other. The crystals seem to belong to the monoclinic system. The melting point is 104° – 105° , and if heated to 160° the substance becomes dark red and gives off gas. It is essentially insoluble in cold water, very slightly soluble in hot; insoluble in ligroin; slightly soluble in ether; not very soluble in cold, freely in hot ethyl or methyl alcohol; freely in benzol, carbonic disulphide, or glacial acetic acid; very freely in chloroform or acetone. Hot alcohol is the best solvent for it. Strong hydrochloric acid has no action upon it, even when the substances are warmed together in open vessels; it is probable, however, that in sealed tubes the same decomposition would take place as that observed with the corresponding dinitro body. Strong sulphuric acid dissolves a little in the cold, more when hot, forming a colorless solution. Strong nitric acid has little or no action in the cold, but, if warmed with it, converts it into an intensely red viscous substance swimming in the red acid liquid, which by further action of strong nitric acid becomes solid and crystalline. A fuller discussion of the action of strong nitric acid and that of dilute sulphuric acid will be found later in this paper.

As was to be expected from the position of one of its hydrogen atoms on a carbon surrounded by two carboxylester radicals and a trinitrophenyl group, the substance possesses marked acid properties. Sodid hydrate in excess gives only a pale red color with the solid ester, owing to the very slight solubility of the sodium salt in sodid hydrate, but upon adding water the coloration increases, and the addition of a few drops of alcohol produces a very dark red solution. Potassic carbonate in aqueous solution gives a slight red color, on the addition of a little alcohol a dark

red solution; acid sodic carbonate acts in much the same way, but the color produced by the aqueous solution is paler than that given with potassic carbonate. Ammonic hydrate gives a red color at once, but this cannot be obtained free from ammonia by evaporation on the water-bath or by using an excess of the ester. The behavior of such a solution made by using an excess of the ester with ammoniac hydrate was studied nevertheless, and the following are the more characteristic precipitates which were obtained:

Magnesium salt, pale rust-colored.

Calcium salt, pale red flocks.

Strontium salt, like that obtained from calcium, but not so heavy a precipitate.

Barium salt, an even less heavy precipitate than that obtained with strontium, also less flocculent.

Manganese salt, yellowish brown.

Zinc salt, pale red.

Cobalt or Nickel salts, yellowish.

Ferric salt, rust-colored.

Cupric salt, a rusty red to orange.

Mercuric chloride, yellowish brown.

Mercuric nitrate, rust-colored.

Mercurous salt, rusty precipitate mixed with the black product from the excess of ammoniac hydrate.

Cadmium salt, yellowish red.

Lead salt, brilliant rust-color.

Silver salt, vivid brown ("Bismarck brown").

The most characteristic point in its behavior with reagents is that the magnesium and calcium salts are less soluble than the strontium and barium salts, the order of solubility being magnesium and calcium least soluble, strontium more soluble, barium the most soluble. A similar observation has been made by Bischoff¹ in regard to the salts of orthonitrobenzoylmaleic ester, and the bromdinitrophenylacetic ester also exhibits the same peculiarity, as we mention in detail in the next paper of this series.

Salts of Bromtrinitrophenylmaleic Ester.

We had intended at first to make a rather thorough study of the salts of the bromtrinitrophenylmaleic ester, but after a few

¹ Ann. Chem. (Liebig) 251, 362.

experiments became convinced that this would be a waste of time, as, owing to the ease with which the atom of bromine can be removed, no very satisfactory analytical results could be obtained; and we were the more ready to give up this part of the work, because our investigation of the secondary oily product of the reaction, by which the bromtrinitrophenylmalonic ester is formed, had settled beyond a doubt the composition of the ester, which before this and the similar investigation made by one of us and W. S. Robinson had rested principally on the analyses of its salts (see this Journal **II**, 97, 1889). We have confined ourselves therefore to a single analysis of the sodium salt, and a preliminary study of the copper salt, the results of which are given below.

Sodium Salt, $C_6HBr(NO_2)_3CNa(COOC_2H_5)_2$.—This substance was made in two ways. First, by digesting solid pure sodic carbonate with a solution of bromtrinitrophenylmalonic ester in absolute alcohol. The red solution was filtered from the excess of sodic carbonate, evaporated to dryness on the water-bath, and dried at 100° , when it gave the following result on analysis:

0.2373 gram of the salt gave after being heated with sulphuric acid 0.0418 gram of sodic sulphate.

	Calculated for $C_6HBr(NO_2)_3CNa(CO_2C_2H_5)_2$.	Found.
Sodium	4.87	5.71

The bad result is probably due to a slight excess of sodic carbonate, which dissolved in the alcohol. The salt looked black and somewhat decomposed.

The second and better method was that used for making the salt of the corresponding dinitro compound, that is, by the action of an alcoholic solution of sodic hydrate or ethylate on an alcoholic solution of the ester, taking care that the ester is in excess. For the necessary precautions see this Journal **II**, 100, 1889. No analysis was made of this preparation, as from our experience with the acetacetic compound we were sure that no accurate analytical results would be obtained.

Properties.—The sodium salt forms an amorphous blackish red mass, soluble in ethyl or methyl alcohol, water, or acetone; tolerably soluble in ether; slightly in chloroform; insoluble in benzol or ligroin. All the solutions have a deep blood-red color. When the salt is treated with an excess of strong nitric acid (of specific gravity 1.36), it is at first decolorised, but almost immedi-

ately turns vivid red, owing to the formation of the substance produced by warming the free ester with nitric acid. This behavior is characteristic, as it appears with none of the similar substances which we have studied.

Copper Salt.—We took up the study of this salt in the hope of throwing light on the composition of the ester, but after analysing several samples were convinced that the precipitate had a varying composition, and therefore describe our work only because of a curious observation made in the course of it. The salt was made by adding a solution of cupric sulphate to an alcoholic solution of the sodium salt, which need not be free from sodic hydrate; the copper salt was extracted with ether, and obtained on evaporating the ethereal solution as an orange mass, which when heated exploded with a blue flame. It was insoluble in water, nearly insoluble in cold alcohol, soluble in hot, and the yellow solution deposited the salt in rhombic crystals; very soluble in benzol or chloroform, insoluble in ligroin.

We next substituted an alcoholic solution of cupric chloride for the cupric sulphate, in hopes of getting a better result, when to our surprise a product was obtained crystallising from alcohol in long white prisms, and melting in the crude state at 75° . This product was obtained more than once, but as frequent crystallisation was necessary to purify it, we did not at first have enough to bring it into a state fit for analysis; and, on returning to the subject after some months, we obtained under the same conditions nothing but the orange explosive copper salt. Unfortunately, we had postponed work on this subject till so near the end of the term that we were unable to give it the careful study it seems to deserve, but its investigation will be continued in this laboratory next year.

Study of the Reactions by which Bromtrinitrophenylmalonic Ester is formed.

The reactions by which the bromtrinitrophenylmalonic ester is formed from the tribromtrinitrobenzol must consist in the replacement of one of the atoms of bromine by the malonic ester radical $\text{CH}(\text{COOC}_2\text{H}_5)_2$, and of another by hydrogen. The first of these processes needs no explanation, but the mechanism of the second, the replacement of the bromine by hydrogen, could be made out only by experiment. Obviously, the first point to be settled was

the form in which the bromine was eliminated ; that is, whether as sodic bromide alone, or partly as sodic bromide and partly as an organic compound. For this purpose the following quantitative determinations were made :

I. 10 grams of tribromtrinitrobenzol, treated with the sodium malonic ester from 15 grams of malonic ester, gave after standing two days and a half 8.83 grams of argentic bromide, corresponding to 3.76 grams of bromine.

II. The same weights under the same conditions gave 9.08 grams of argentic bromide, corresponding to 3.86 grams of bromine.

If two atoms of bromine had been removed, the amount of bromine should have been 3.55 grams. Therefore the percentages of the theoretical bromine removed as sodic bromide were,

I.	II.
105.9	108.8

It appears, therefore, that a little more than the amount calculated for two atoms of bromine has been removed as sodic bromide, and this is easily explained by the observation described later in this paper, that sodium malonic ester can act on the bromtrinitrophenylmalonic ester even in the cold to form the trinitrophenylenedimalonic ester, a small quantity of which was undoubtedly formed in these two experiments by the large excess of sodium malonic ester present. At any rate, there can be no question that all the bromine was removed in the form of sodic bromide.

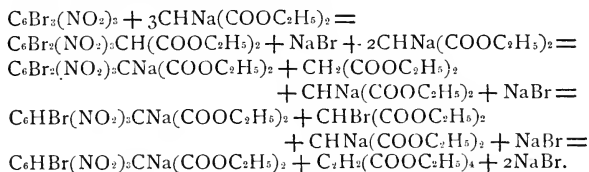
The next step consisted in determining the nature of the organic secondary product. For this purpose, the oil, separated from the bromtrinitrophenylmalonic ester by sucking out the crude product on the pump and treatment with alcohol, was allowed to stand till it ceased to deposit crystals of the ester, and then submitted to distillation under diminished pressure. The pressure varied from 22 to 25 mm., and a distillate began to appear when the thermometer inside the flask stood at 98° , and was collected until the temperature had reached 160° , when about one-third of the total volume had passed over. In this way a clear yellow liquid was obtained, which distilled unaltered at ordinary pressure between 197° and 206° . We therefore inferred it was mostly malonic ester, boiling point 197.7° , a view of its nature which was confirmed by its smell. As the whole of the distillate passed over below 206° , there could be no large amount of tartronic ester (boiling point 220°) present, which we had expected after the work of one of us and

W. S. Robinson on the corresponding dinitro compound, and the secondary product of the reaction must be looked for in the residue which had been left behind in the flask after the distillation under diminished pressure. This was a thick blackish brown oil, which on standing for about a week deposited crystals all over its surface; these were removed and allowed to stand on filter paper until a large part of the oil had been sucked out, when they were purified by washing with a small quantity of cold alcohol, and then crystallising from boiling alcohol, until they showed the constant melting point 76° . The substance formed long glittering colorless needles or prisms, and contained no bromine: we decided accordingly that it was the acetylentetracarboxylic ester (melting point 76°), and this conclusion was confirmed by the following analysis:

0.2270 gram of the substance gave on combustion 0.4384 gram of carbonic dioxide and 0.1506 gram of water.

	Calculated for $C_2H_2(CO_2C_2H_5)_4$.	Found.
Carbon	52.83	52.67
Hydrogen	6.92	7.36

The amount of acetylentetracarboxylic ester was so considerable that there can be no doubt it was a principal product of the reactions by which the bromtrinitrophenylmalonic ester is formed, and these must therefore be written thus:



The only objection which could be urged against this series of reactions is that the yield of bromtrinitrophenylmalonic ester is only 64 per cent. of the theoretical, from which it might be argued that nearly half of the tribromtrinitrobenzol may have undergone some different transformation. This objection is disposed of, however, by the fact that W. D. Bancroft and one of us have succeeded in getting a yield of 80 per cent. of the dibromdinitrophenylmalonic ester from tetrabromdinitrobenzol by a series of reactions exactly analogous to those just given. The missing 36 per cent. of the

bromtrinitrophenylmalonic ester must therefore have remained dissolved in the oil, and have been destroyed by the distillation even under the diminished pressure used by us.

Action of Nitric Acid.

The intense red color produced by the action of nitric acid of specific gravity 1.36 on the sodium, or copper salt of the bromtrinitrophenylmalonic ester in the cold, or on the ester itself at 100°, seemed to us of great interest, and we laid out what we thought would be time enough for its investigation; unfortunately, however, this was not the case, since, after the work had been going on for some time, we found that at least two substances were formed by this reaction, and consequently the end of the term surprised us before we had reached any definite results. We have decided, however, to publish here what results we have obtained, as we are unable to go on with this work together, but wish it to be understood that all these statements are to be taken as preliminary.

If about 1 gram of bromtrinitrophenylmalonic ester was mixed with 2-3 cc. of strong nitric acid (specific gravity 1.36), no change took place in the cold; but if the mixture was warmed gently on the water-bath for less than five minutes, an intense vivid red color appeared in both the acid liquid and the organic substance, which melted and became converted into a viscous mass. If now the acid was poured off, a fresh quantity added, and the gentle warming repeated, the viscous drop became converted into a red crystalline mass, and by continuing this treatment with successive portions of nitric acid the red color could be removed partially, so that the product had a spotted red and white appearance. This frequent treatment with nitric acid was, however, unnecessary, as the red crystalline product after the second warming with nitric acid gave, when crystallised from alcohol, well formed white prisms and a reddish mother liquor. The red nitric acid poured off from the principal part of the product gave with water a red precipitate, but a better mode of treatment seemed to be to evaporate this red acid to dryness on the water-bath. The residue, or precipitate obtained with water, was partly viscous, partly crystalline, and by treating it again with warm strong nitric acid a new quantity of the red crystalline substance was obtained, but the amount recovered in this way was so small that it hardly paid for

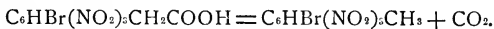
the trouble. The white crystals, after purification by crystallisation from alcohol, showed the constant melting point 125° , and their behavior in melting was very characteristic, as they turned from white to bright red, and swelled to many times their original volume. They were not affected by sodic hydrate in aqueous solution. Supposing that the substance was homogeneous because of its constant melting point, we analysed it, but on studying its properties more carefully we began to doubt its purity, for the following reasons: First. Although the microscopic examination showed that the substance consisted principally of white, short, rather thick monoclinic prisms, usually with both terminations well developed and made up of two planes, there were mixed with these longer prisms, and we could not decide whether these latter were a different substance or merely a different habit of the same. Second. When the crystals were treated with sodic hydrate and alcohol a little of a soluble red salt was formed around each crystal, but we could not convert the whole of the crystals into this salt. This seemed to point to the presence of an impurity, from which the salt was formed. Third. We found, almost at the very end of the term, that by warming the bromtrinitrophenylmalonic ester with strong nitric acid for three hours, instead of a few minutes, a red substance was obtained which crystallised from alcohol, became white, and melted at 156° instead of 125° , and, what was as distinctive as the different melting point, fused to a colorless liquid, and gave a red solution with aqueous sodic hydrate. This substance was discovered so late that we had no time to investigate it, but some of it seemed to be formed even on shorter heating (15 minutes) with the nitric acid. For these reasons we have decided that it is wiser to postpone the publication of our analyses of the substance melting at 125° until the work has been repeated with samples in regard to the purity of which there can be no doubt. We add such results of our work as are established with certainty. The analyses made by us showed that there were three atoms of nitrogen to one of bromine in the substance, and therefore the action of the nitric acid did not consist in the introduction of another nitro, or nitroso group. The fact that it is insoluble in aqueous sodic hydrate shows that it is not a free acid, and its action with hydrochloric acid would indicate that it was an ester, as, when heated to 135° – 140° with this acid in a sealed tube for 36 hours, a gas was given off burning with a green-bordered flame, and giving a white precipitate

with lime-water, which therefore must have contained ethyl chloride and carbonic dioxide. The solid product of this action was partly viscous and partly crystalline; the latter melted in the crude state above 180° . It has been stated already that the substance melting at 125° turns red and increases in volume when it melts; this change, which takes place to a limited extent even when it is kept at 100° for some time, is accompanied by loss of weight, as a sample kept at its melting point for some days lost at least 17 per cent., and gave a residue consisting of two or more substances, one white and crystalline, the other red and viscous.

Action of Sulphuric Acid.—Constitution of the Bromtrinitrophenylmalonic Ester.

The action of dilute sulphuric acid upon the bromtrinitrophenylmalonic ester was studied in the hope of obtaining the as yet unknown bromtrinitrophenylacetic acid, as it had been found by one of us and W. S. Robinson¹ that the corresponding dinitro compound was decomposed in this way. For this purpose, about 2 grams of the ester were boiled in a flask under a return condenser with sulphuric acid of specific gravity 1.44 and boiling point 132° until the ester had dissolved; the liquid was then allowed to cool, when it deposited crystals, which, after recrystallisation from alcohol, were recognised by their melting point 143° – 144° , their appearance, and the absence of acid properties, as the metabromtrinitrotoluol discovered in this laboratory by Bentley and Warren.

It is evident therefore that the bromtrinitrophenylacetic acid is less stable than the corresponding dinitro compound, as indeed was to be expected, and was broken up as soon as formed into the substituted toluol and carbonic dioxide, according to the following reaction:



The formation of this substance would settle the constitution of the bromtrinitrophenylmalonic ester, if that were necessary, but the preparation of the ester from symmetrical tribromtrinitrobenzol leaves no doubt as to its constitution, which must be as follows, $\text{CH}(\text{COOC}_2\text{H}_5)_2$, NO_2 , Br, NO_2 , H, NO_2 , 1, 2, 3, 4, 5, 6, and Bentley and Warren have established the corresponding constitution for their substituted toluol.

¹ This Journal 11.

Trinitrophenylendimalonic Ester, $C_6H(NO_2)_3[CH(COOC_2H_5)_2]_2$.

This substance was formed by the further action of sodium malonic ester on bromtrinitrophenylmalonic ester. For this purpose, 1 gram of bromtrinitrophenylmalonic ester dissolved in ether was mixed with 1.5 gram of malonic ester previously converted into sodium malonic ester and dissolved in much absolute alcohol, and the mixture boiled in a flask with a return condenser for an hour. The product, which was very dark brown, almost black, was treated with water, acidified with dilute sulphuric acid avoiding a large excess, the ether removed with a drop funnel, and the aqueous liquid shaken out twice with ether. The extract, after distilling off the ether and allowing it to get perfectly cool, was treated with a little alcohol, when crystals separated on standing, which were purified by recrystallisation from alcohol, until they showed the constant melting point 123° . They gave no test for bromine when heated on a copper wire, and, after drying *in vacuo*, were analysed with the following results:

I. 0.3004 gram of the substance gave on combustion 0.5043 gram of carbonic dioxide and 0.1230 gram of water.

II. 0.2392 gram of the substance gave 16.8 cc. of nitrogen at a temperature of 25° and a pressure of 768 mm.

	Calculated for $C_6H(NO_2)_3[CH(COOC_2H_5)_2]_2$.	I. Found.	II.
Carbon	45.37	45.78	
Hydrogen	4.35	4.55	
Nitrogen	7.94		7.92

A small quantity of this substance can also be formed in the cold, and more than once some of it has been obtained in making the bromtrinitrophenylmalonic ester by the process described earlier in this paper.

Properties.—The trinitrophenylendimalonic ester crystallises from alcohol in long colorless prisms, terminated by a single rhombic plane at a tolerably sharp angle to the sides; less frequently, the termination consists of two planes at an obtuse angle to each other, so that the general effect is as if the prisms had rounded ends. They are frequently grouped, or twinned, parallel to their long axes, so that often there are two or more terminations at one end of a group. The substance melts at 123° , and is very nearly, if not quite, insoluble in water, whether cold or boiling; essentially insoluble in ligroin; not very soluble in cold ethyl or

methyl alcohol, freely in either of these solvents when hot; very slightly soluble in carbonic disulphide; soluble in ether or glacial acetic acid, and freely soluble in benzol, chloroform, or acetone. Its acid properties are not so strongly developed as we expected. An aqueous solution of sodic hydrate turns the solid pale red, but does not dissolve it to any extent; if, however, solid hydrate is added to its alcoholic solution, it at once takes on a dark brownish red color, much browner than any of the similar salts which we have studied—in fact it would be possible to recognise the salt by this color. An aqueous solution of potassic carbonate gives a very faint red color with it, which is increased, but not to a great extent, by adding alcohol to the aqueous solution. The action was incomplete at best; acid sodic carbonate had no action on it in aqueous solution, but on the addition of alcohol a barely perceptible red color appeared. Ammonic hydrate even in dilute aqueous solution dissolved it easily with a brown color; the solution turned blacker when the attempt was made to drive off the excess of ammonia on the water-bath, and a white scum formed on the surface, probably the original substance. The behavior of this solution was studied with some of the commoner reagents; but, as it showed such evident signs of decomposition, we did not think it worth while to extend this work to salts of all the basic radicals.

Ferric salt, cupric salt, silver salt, and lead salt all gave brown flocculent precipitates.

Calcium salt gave no precipitate.

Barium salt, a very slight dirty brown precipitate, but none if the solution had not been warmed on the water-bath in the vain attempt to drive off the excess of ammonia.

Strong sulphuric acid dissolved the dimalonic ester, giving a colorless solution. Strong hydrochloric acid had no action upon it, whether hot or cold. Strong nitric acid dissolved it partially in the cold, giving a yellowish solution, which when warmed became darker yellow; but if the warming on the water-bath was continued for some time, the acid liquid became red, and a red viscous substance was also obtained, which, after washing with water and crystallisation from alcohol, was converted into yellow plates melting at 104° – 105° in the crude state. It is evident that the action here is similar to that of bromtrinitrophenylmalonic ester with strong nitric acid, but the end of the term has prevented us from continuing the study of this substance at present.

LXVII.—ON CHLORPYROMUCIC ACIDS.¹

BY HENRY B. HILL AND LOUIS L. JACKSON.

Many years ago Malaguti² found that dry chlorine gas was quickly absorbed by ethyl pyromucate, and that a thick viscous liquid was formed, the composition of which showed that four atoms of chlorine had been taken up. The oil was carbonised on distillation, and yielded with potassic hydrate decomposition products which were not further studied. Although Schmelz and Beilstein³ later found that chlorine converted pyromucic acid in aqueous solution into mucochloric acid, and this reaction was afterwards further studied by Hill and Bennett,⁴ no further experiments, as far as we could learn, had ever been made with dry chlorine on pyromucic acid or its ethers. In 1884, after it had been shown by investigations carried on in this laboratory that substitution products could readily be formed from pyromucic acid by the action of dry bromine, Mr. J. N. Garratt, at that time an assistant in the laboratory, undertook the investigation of the action of dry chlorine under similar conditions. Although he succeeded in isolating a dichlorpyromucic acid melting at 167°–168° in a state of purity, he found that the reaction differed in many respects from the corresponding reaction with bromine, and that the matter deserved a more careful study than he was then able to bestow upon it. Mr. Garratt relinquished his investigation of this subject in order to continue his studies in Zurich, and in the following winter met with the fatal accident which so sadly ended his promising career.

The observations which already had been made interested us so much that in 1886 we undertook a more thorough study of the subject. We had already collected a great deal of material which we did not think it necessary to publish in a preliminary form, when Denaro⁵ published in the *Gazzetta Chimica* a brief notice of a dichlorpyromucic acid melting at 167°–168°, which was evidently identical with that prepared by Garratt. The paper contained a description of the acid and two of its salts, but the

¹ Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences. A part of the work described in the following paper was presented in the form of a thesis to the Academic Council of Harvard University, in May, 1888, by Louis L. Jackson, then candidate for the degree of Doctor of Philosophy.

² *Ann. Chim. Phys.* **64**, 282; **70**, 371.

³ *Ann. Chem. (Liebig)*, Suppl. **3**, 276.

⁴ *Ber. d. chem. Ges.* **12**, 655.

⁵ *Gazz. chim. ital.* **16**, 333.

analyses of the latter did not agree with those which we had already obtained, and moreover contained such serious misprints or arithmetical errors, or both, as to be wholly without value. In consequence of the appearance of that paper, we thought it best to publish a preliminary account¹ of our work, so far as that one acid was concerned, more especially since our study of it was then essentially completed.

In repeating the experiments of Garratt, we had no difficulty in isolating the dichlorpyromucic acid which he had prepared, but we found that the reaction was still more complex than we had supposed. At ordinary temperatures chlorine was rapidly absorbed, but the pyromucic acid was soon so coated with the viscous addition-product that a homogeneous product could not be obtained. On heating, the reaction could easily be pushed to the end, and the gain in weight closely corresponded with the addition of four atoms of chlorine. At the same time hydrochloric acid and carbonic dioxide were given off, and the resulting product contained a percentage of chlorine much larger than that demanded by any simple addition-product. Under these circumstances it seemed advisable to return to the ethyl pyromucic tetrachloride of Malaguti, which, from his description and analyses, appeared to be homogeneous; and to take up the study of the more complex action of chlorine upon the acid itself after this investigation had made us better acquainted with some of the products likely to be formed. Although we were unable to prepare a perfectly homogeneous product by following the directions of Malaguti, we found no difficulty in so modifying the conditions that the resulting compound should give us pure $\beta\gamma$ -dichlorpyromucic acid melting at 168° – 169° , δ -chlorpyromucic acid melting at 176° – 177° , or trichlorpyromucic acid melting at 172° – 173° . The $\beta\delta$ -dichlorpyromucic acid we were unable to prepare by direct substitution, or by saponification of ethyl pyromucic tetrachloride; but by distillation of ethyl pyromucic tetrachloride, of the tetrachloride of pyromucyl chloride, or of ethyl δ -chlorpyromucic tetrachloride, the $\beta\delta$ -dichlorpyromucic acid melting at 155° – 156° may be obtained, and in the first two cases a third dichlorpyromucic acid melting at 197° – 198° is also formed. By careful reduction of the $\beta\delta$ - or the $\beta\gamma$ -dichlorpyromucic acids, the β -chlorpyromucic acid melting at 145° – 146° is formed.

¹ Ber. d. chem. Ges. **20**, 252.

ETHYL PYROMUCIC TETRACHLORIDE.

The ethyl pyromucate which we have used in the course of our investigations we have made by warming a solution of pyromucic acid (3 parts) in absolute alcohol (5 parts) with concentrated sulphuric acid (3 parts acid, sp. gr. 1.84). After heating for four hours on the water-bath, the mixture was allowed to cool, precipitated with water, and the ether washed with a dilute solution of sodic carbonate. The crude ether was then dried by exposure to the air and distilled. The yield of pure distilled ether which is thus obtained amounts to about 85 per cent. of the weight of the acid taken. This is somewhat less than that which may be obtained by means of hydrochloric acid, but the method is much more expeditious and convenient.

When dry chlorine is passed over ethyl pyromucate we found that the ether was rapidly liquefied with the evolution of heat, and that the formation of the addition-product proceeds as described by Malaguti until the ether has increased in weight very nearly the amount required by the addition of four atoms of chlorine. We soon found, however, that, no matter how carefully the chlorine was dried, hydrochloric acid escaped, showing the formation of a substitution product, and that the amount of hydrochloric acid formed depended largely upon the rapidity of the stream of chlorine and the consequent elevation of temperature. Even when the ether was carefully cooled to 0° during the whole of the treatment with chlorine, the formation of hydrochloric acid could not wholly be avoided. In this respect our experience agrees with that of Hill and Sanger,¹ who were unable to form the ethyl pyromucic tetrabromide without the simultaneous formation of substitution products. While the statements of Malaguti seemed to leave no room for doubt that the ethyl pyromucic tetrachloride was completely carbonised by heat, experiments made with bromine in this laboratory had shown that substitution products could readily be formed from the ethyl pyromucic tetrabromide by heat, and it seemed to us hardly conceivable that complete carbonisation should ensue. A preliminary trial showed so much less charring under ordinary pressure than we had anticipated, that we were encouraged to hope that the ethyl pyromucic tetrachloride itself might be distilled under diminished pressure without essential decomposition. Ethyl pyromucate was there-

¹ Proc. Am. Acad. 21, 155.

fore carefully treated with chlorine at 0° until it ceased to gain in weight. Hydrochloric acid was given off in small quantity, and the total gain in weight was 94 per cent. of the weight of ethyl pyromucate taken, instead of the theoretical gain of 101 per cent. The product was then fractionally distilled under a pressure of 15 mm., and showed its complex nature by the wide range of its boiling point, 104° – 160° . Above 160° there remained a residue which, even under 15 mm. pressure, could not be distilled without decomposition.

None of the fractions showed any tendency to solidify in a freezing mixture. After several distillations, it became evident that the greater portion boiled without essential decomposition between 150° – 160° , and that smaller portion boiled below 110° .

In order to determine the nature of the several products, the following analyses were made. Each fraction was collected under 15 mm. pressure.

A. Boiling point 104° – 110° ; weight = 2.6 grams.

0.2235 gram substance gave 0.2139 gram AgCl.

Cl	Calculated for $C_5H_7ClO_3C_2H_5$.	Found.
	20.34	23.63

B. Boiling point 145° – 150° ; weight = 3.2 grams.

0.2334 gram substance gave 0.4418 gram AgCl.

C. Boiling point 152° – 153° ; weight = 7.7 grams.

I. 0.1678 gram substance gave 0.3431 gram AgCl.

II. 0.1415 gram substance gave 0.2889 gram AgCl.

D. Boiling point 153° – 157° ; weight = 12.0 grams.

0.1502 gram substance gave 0.3094 gram AgCl.

Cl	Calculated for $C_5H_3O_3C_2H_5Cl_4$.	Found.			
		B.	I. C.	II.	D.
	50.36	46.77	50.55	50.49	50.97

From these analyses it was evident that the fraction C consisted of pure ethyl pyromucic tetrachloride; the fraction D contained a slight admixture of a product containing a higher percentage of chlorine; the fraction A approached in composition the ethyl chlorpyromucate; while the fraction B was a mixture. In order to be quite sure of the correctness of our conclusions, we treated these successive fractions with an alcoholic solution of sodic hydrate, and obtained acids in each case confirming the results of

our analyses. From fraction A we obtained an acid crystallising from hot water in irregular leafy plates which melted at 176° – 177° . The physical properties and melting point were sufficient to identify this acid as the δ -chlorpyromucic acid later described, and to prove that the lower boiling fraction consisted chiefly of ethyl δ -chlorpyromucate. Fraction C yielded us without difficulty, and in nearly theoretical quantity, an acid which, when recrystallised twice from benzol, melted sharply at 168° – 169° , and in other respects proved to be identical with the $\beta\gamma$ -dichlorpyromucic acid which we shall hereafter fully describe. The formation of this acid in nearly theoretical quantity and without recognisable admixture proves that the fraction C consisted of pure ethyl pyromucic tetrachloride. Fraction D yielded us a somewhat less pure $\beta\gamma$ -dichlorpyromucic acid, as did also fraction B. In the latter case, however, we were able to isolate a small quantity of a sparingly soluble acid, crystallising from water in minute needles which closely resembled trichlorpyromucic acid. It was therefore evident that the main product formed by the action of chlorine at 0° upon ethyl pyromucate was the tetrachloride, and this might be distilled under diminished pressure without essential decomposition. At the same time it was shown that substitution was effected even in the cold, and that the product contained ethyl δ -chlorpyromucate and very possibly its tetrachloride.

δ -CHLORPYROMUCIC ACID.

Since substitution had taken place at low temperatures, it seemed not unlikely that at 100° the substitution might be so rapid as to offer a convenient mode for the preparation of chlorpyromucic acids. Ethyl pyromucate, when treated with bromine at 100° , yields δ -brompyromucic and $\beta\delta$ -brompyromucic acids still more readily than pyromucic acid itself. We accordingly passed dry chlorine through ethyl pyromucate heated to 100° , but found that a higher temperature was necessary in order that the substitution might promptly be effected. At 145° the action was sufficiently rapid, and the chlorine was passed through the melted ether at this temperature until a gain in weight was noted which corresponded to the substitution of one hydrogen atom by chlorine. The viscous liquid which was thus obtained was then slowly added to an excess of a concentrated alcoholic solution of sodic hydrate, care being taken to avoid any great elevation of temper-

ature. When the action was completed the sparingly soluble sodium salt was removed by filtration and dried. The alcoholic filtrate contained small quantities of this sodium salt in solution, and contained further a small amount of some volatile furfuran compound. We converted the excess of sodic hydrate into carbonate with carbonic dioxide, removed the sodic carbonate by filtration, and distilled the alcoholic filtrate. The distillate when mixed with water threw down a minute quantity of a colorless oil of peculiar aromatic odor, which we have as yet been unable to identify through lack of material. The small amount of sodium salt obtained from the alcoholic mother liquors was then added to the main portion. The sodium salt when dissolved in water and acidified with hydrochloric acid then yielded the crude δ -chlorpyromucic acid, which not infrequently needed no other purification than recrystallisation from benzol. If, however, the treatment with chlorine had been too long continued, or the action had taken place at too low a temperature, the product contained dichlorpyromucic and trichlorpyromucic acids which could not be removed by simple recrystallisation. Whenever the crude acid failed on trial to crystallise from hot water in shining irregular plates, it was necessary to resort to chemical means for its purification. The acid was suspended in twenty times its weight of cold water, ammonia added in slight excess, and then baric chloride in quantity sufficient to precipitate the sparingly soluble barium salts of the admixed acids. After the separation of these salts is complete, the filtered solution gives on acidification an acid which crystallises from water in leafy plates, and which may further be purified by recrystallisation from benzol. The yield of chlorpyromucic acid thus obtained amounts to about 40 per cent. of the weight of ether taken, or 38 per cent. of the theoretical amount.

I. 0.2761 gram substance gave 0.4145 gram CO_2 and 0.0494 gram H_2O .

II. 0.2667 gram substance gave 0.2642 gram AgCl .

III. 0.2990 gram substance gave 0.2950 gram AgCl .

	Calculated for $\text{C}_8\text{H}_9\text{ClO}_3$.	I.	Found. II.	III.
C	40.96	40.94
H	2.05	1.99
Cl	24.23	...	24.49	24.39

The δ -chlorpyromucic acid is readily soluble in hot water, sparingly in cold water, and crystallises in large irregular leafy plates, which closely resemble the corresponding bromine derivative. It dissolves readily in alcohol, ether, or hot benzol, but sparingly in cold benzol. The acid recrystallised from benzol melted at 176° – 177° , and a preparation made from the pure ethyl ether melted at the same point. Its solubility in cold water was determined according to the method of V. Meyer. A weighed portion of the solution saturated at 19.5° was boiled with baric carbonate, and the barium dissolved determined by precipitation with sulphuric acid.

I. 37.8458 grams solution saturated at 19.5° gave 0.0833 gram BaSO_4 .

II. 33.5216 grams solution saturated at 19.5° gave 0.0742 gram BaSO_4 .

According to these determinations, the solution saturated at 19.5° contained the following percentages of acid :

I.	II.
0.28	0.28

Baric δ -chlorpyromucate, $\text{Ba}(\text{C}_5\text{H}_2\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$.—The barium salt was prepared by boiling the acid with an excess of baric carbonate. The salt is quite readily soluble even in cold water, still more readily soluble in hot water, and separates from a hot concentrated solution in thin leafy plates, usually aggregated in globular form. The air-dried salt contains one molecule of water, which it loses rapidly at 100° .

I. 1.2193 gram air-dried salt lost at 100° 0.0491 gram H_2O .

II. 0.5932 gram air-dried salt gave 0.3094 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_5\text{H}_2\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$.	I.	Found.	II.
H_2O	4.04	4.04
Ba	30.72	...	30.67	...

0.6909 gram salt dried at 100° gave 0.3763 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_5\text{H}_2\text{ClO}_3)_2$	Found.
Ba	32.01	32.02

The solubility of the salt in cold water was determined according to the method of V. Meyer.

I. 9.3523 grams solution saturated at 19.5° gave 0.2932 gram BaSO_4 .

II. 8.3395 grams solution saturated at 19.5° gave 0.2534 gram BaSO_4 .

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt :

I.	II.
5.76	5.58

Calcic δ -chlorpyromucate, $\text{Ca}(\text{C}_6\text{H}_2\text{ClO}_3)_2 \cdot 3\text{H}_2\text{O}$.—The calcium salt was prepared by boiling the acid with an excess of calcic carbonate. It is readily soluble in hot water, rather sparingly soluble in cold water, and separates from a hot concentrated solution in clustered prisms with rectangular terminations. The air-dried salt contains three molecules of water. It effloresces slowly over sulphuric acid, and loses all its water readily at 100° .

I. 1.0814 gram air-dried salt lost at 100° 0.1480 gram H_2O .

II. 1.2247 gram air-dried salt lost at 100° 0.1689 gram H_2O .

	Calculated for $\text{Ca}(\text{C}_6\text{H}_2\text{ClO}_3)_2 \cdot 3\text{H}_2\text{O}$.	I.	Found.	II.
H_2O	14.03	13.70		13.79

I. 0.6236 gram salt dried at 100° gave 0.2564 gram CaSO_4 .

II. 0.5509 gram salt dried at 100° gave 0.2244 gram CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_6\text{H}_2\text{ClO}_3)_2$.	I.	Found.	II.
Ca	12.09	12.09		11.98

The solubility of the salt in cold water was determined according to the method of V. Meyer. The calcium was precipitated as oxalate, and the oxalate ignited with sulphuric acid.

I. 21.6494 grams solution saturated at 19.5° gave 0.1002 gram CaSO_4 .

II. 17.7467 grams solution saturated at 19.5° gave 0.0809 gram CaSO_4 .

The solution saturated at 19.5° contained therefore the following percentages of anhydrous salt :

I.	II.
1.13	1.11

Potassic δ -chlorpyromucate, $\text{KC}_6\text{H}_2\text{ClO}_3$.—The potassium salt is readily soluble even in cold water, and separates from a hot concentrated solution on rapid cooling in fine branching needles; on slower cooling, in small thin oblique plates. The salt lost nothing in weight when dried at 120° , and analysis showed it to be anhydrous.

- I. 0.6543 gram salt dried at 120° gave 0.3100 gram K_2SO_4 .
 II. 0.6390 gram salt dried at 120° gave 0.3018 gram K_2SO_4 .

	Calculated for $KC_5H_2ClO_3$.	I.	Found.	II.
K	21.18	21.27		21.20

Argentio δ -chlorpyromucate, $AgC_5H_2ClO_3$.—The silver salt may best be prepared by precipitating a solution of the barium salt with argentic nitrate.

For analysis the precipitated salt was well washed, recrystallised from hot water, and dried *in vacuo* over sulphuric acid. It is sparingly soluble even in hot water, and separates from a hot concentrated solution in irregularly branching flattened needles.

- I. 0.4843 gram substance gave 0.2730 gram $AgCl$.
 II. 0.3948 gram substance gave 0.2220 gram $AgCl$.

	Calculated for $AgC_5H_2ClO_3$.	I.	Found.	II.
Ag	42.60	42.44		42.34

Ethyl δ -chlorpyromucate, $C_5H_2ClO_3C_2H_5$.—The ethyl ether was prepared by heating at 100° a solution of 5 parts of δ -chlorpyromucic acid in 10 parts of absolute alcohol, with the addition of 5 parts of concentrated sulphuric acid (sp. gr. 1.84).

After heating for three hours, the ether was precipitated by the addition of water, washed first with dilute sodic carbonate, then with water, and finally dried with calcic chloride. The ether is a colorless heavy oil boiling at 216° – 218° (column completely in vapor) under a pressure of 76.8 mm., solidifying at 1° – 2° , and melting at the same point.

- I. 0.2740 gram substance gave 0.2219 gram $AgCl$.
 II. 0.2918 gram substance gave 0.2402 gram $AgCl$.

	Calculated for $C_5H_2ClO_3C_2H_5$.	I.	Found.	II.
Cl	20.34	20.02		20.35

δ -Chlorpyromucamide, $C_5H_2ClO_2NH_2$.— δ -Chlorpyromucic ether is but slowly attacked by concentrated ammonia in the cold, and the amide may more readily be prepared from the acid chloride by means of solid ammonic carbonate. The amide is readily soluble in hot water, sparingly soluble in cold water, and separates from a hot concentrated solution in fine branching needles, which melt at 154° – 155° .

For analysis, the amide was dried over sulphuric acid.

I. 0.1696 gram substance gave 0.1677 gram AgCl.

II. 0.2933 gram substance gave 25.7 cc. moist N at 25° and under a pressure of 764 mm.

	Calculated for $C_6H_2ClO_2NH_2$.	I.	Found.	II.
Cl	24.40	24.44
N	9.62	9.82

Preparation I was made from the ether, and II from the acid chloride.

There seemed no room for doubt that the chlorpyromucic acid thus formed by the direct replacement of hydrogen by chlorine, like the δ -brompyromucic acid obtained in a similar way, contained its chlorine in the δ position. We considered it necessary, however, to establish this point by direct experiment.

Action of Bromine and Water.

Although the action of bromine on δ -brompyromucic acid suspended in water varied greatly with the conditions, Hill and Sanger¹ found that, when the oxidation was carefully conducted, fumaric acid alone was formed. We therefore suspended the δ -chlorpyromucic acid in about twenty-five times its weight of water, and passed in bromine vapor slowly with a current of air. The acid gradually dissolved, and but little more than two molecules of bromine were needed to complete the oxidation. After standing for some time in the cold, the solution was evaporated to a small volume, and the crystalline acid which appeared as the solution cooled recrystallised from hot water. In this way we obtained a white crystalline acid which contained neither chlorine nor bromine, which was sparingly soluble in cold water, more readily in hot water, and which remained unchanged when heated to 200°. Although the acid was thus sufficiently characterised as fumaric acid we further analysed its silver salt.

0.4943 gram substance dried at 120° gave 0.5591 gram AgBr.

	Calculated for $Ag_2C_4H_2O_4$.	Found.
Ag	65.46	64.97

In the oxidation of the δ -chlorpyromucic acid by bromine water, fumaric acid had therefore been formed according to the equation:



¹ Proc. Am. Acad. 21, 144.

Action of Nitric Acid.

δ -Chlorpyromucic acid is not as readily attacked by nitric acid as the δ -brompyromucic acid, and for its complete oxidation we found it necessary to heat one part of the acid with three parts of strong nitric acid (sp. gr. 1.42) diluted with twice its weight of water. After heating for three hours the oxidation was completed, and on evaporation fumaric acid was obtained, which was recognised by its sufficiently characteristic physical properties.

 β -CHLORPYROMUCIC ACID.

Hill and Sanger¹ found no difficulty in preparing β -brompyromucic acid by the reduction of either of the two dibrompyromucic acids described by them. The corresponding dichlorpyromucic acids we found to be much more refractory, and we succeeded in preparing the β -chlorpyromucic acid only after many unsuccessful attempts. The $\beta\gamma$ -dichlorpyromucic acid, which was the more accessible, proved to be the more difficult of reduction, so that almost the whole of the material for this investigation was made from the $\beta\delta$ -dichlorpyromucic acid. When zinc dust is added to a cold ammoniacal solution of this acid, no perceptible reaction takes place, and even after long standing no essential change can be detected. Even when the ammoniacal solution is boiled with a large excess of zinc dust the reduction is but slowly effected, and long continued heating is necessary to complete the reaction. We have found it advantageous to dissolve the acid in about twenty times its weight of dilute ammonic hydrate, to add an equal weight of zinc dust, and to boil for eight or ten hours, taking care to keep the solution strongly ammoniacal. The filtered solution is then cooled and acidified with dilute sulphuric acid, the acid which separates removed by filtration, the filtrate extracted with ether, and the residue left upon the evaporation of the ether added to the main product. The crude acid thus obtained melted at about 130° , and evidently contained unaltered $\beta\delta$ -dichlorpyromucic acid. We therefore dissolved it in dilute ammonic hydrate, and added to the ammoniacal solution calcic chloride as long as a sparingly soluble calcium salt was promptly precipitated. The filtered solution then gave, when acidified with hydrochloric acid, a crystalline acid, which after recrystallisation from hot water

¹ Proc. Am. Acad. 21, 147.

melted at 145° – 146° , and proved upon analysis to be a chlorpyromucic acid. From the sparingly soluble calcium salt, which had been removed by filtration, we obtained only unaltered $\beta\delta$ -dichlorpyromucic acid, which in its turn was treated with zinc dust. In this way we found it possible to obtain from the $\beta\delta$ -dichlorpyromucic acid at least 80 per cent. of the theoretical amount of pure β -chlorpyromucic acid. Zinc dust, even after long boiling, seems to have but little action upon $\beta\gamma$ -dichlorpyromucic acid in ammoniacal solution, but sodium amalgam slowly reduces it at 100° . In order to effect complete reduction, it proved to be necessary to use a large excess of sodium in the form of a one per cent. amalgam, and the reaction was then completed after heating for three hours on the water-bath. The acid obtained by acidification melted at 145° – 146° , contained the percentage of chlorine required by a chlorpyromucic acid, and appeared to be in all respects identical with the acid obtained from the $\beta\delta$ -dichlorpyromucic acid. While the yield of pure acid was in this case but 50 per cent. of the theoretical amount, it is possible that it might be somewhat increased by further experiments. From the third isomeric dichlorpyromucic acid, subsequently described, we have as yet been able to obtain no definite reduction product.

The β -chlorpyromucic acid dried over sulphuric acid gave on analysis the following results:

I. 0.2710 gram substance gave 0.4073 gram CO_2 and 0.0513 gram H_2O .

II. 0.1385 gram substance gave 0.1355 gram AgCl .

III. 0.1736 gram substance gave 0.1692 gram AgCl .

	Calculated for $\text{C}_6\text{H}_3\text{ClO}_3$.	I.	Found. II.	III.
C	40.96	40.99
H	2.05	2.10
Cl	24.23	...	24.18	24.10

Analysis III was made with material prepared from the $\beta\gamma$ -dichlorpyromucic acid.

β -Chlorpyromucic acid is readily soluble in hot water, sparingly soluble in cold water, and crystallises from hot aqueous solution in thin irregular striated plates or flattened prisms. It is readily soluble in alcohol, ether, hot benzol or hot chloroform, and is but sparingly soluble in cold benzol or cold chloroform. When repeatedly crystallised from hot water it melted at 145° – 146° , and

recrystallisation from other solvents failed to raise this melting point.

In order to determine the solubility of the acid in cold water, a weighed quantity of a solution of the acid saturated at 19.8° was boiled with baric carbonate, and the barium taken into solution precipitated as sulphate.

I. 31.6300 grams solution saturated at 19.8° gave 0.2019 gram BaSO_4 .

II. 34.0328 grams solution saturated at 19.8° gave 0.2176 gram BaSO_4 .

The solution saturated at 19.8° therefore contained the following percentages of the acid :

I.	II.
0.80	0.80

For the further characterisation of the acid we prepared certain of its salts.

Baric β -chlorpyromucate, $\text{Ba}(\text{C}_5\text{H}_2\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$.—The barium salt was prepared by boiling a solution of the acid with an excess of baric carbonate. The filtered solution was evaporated, and the salt which separated on cooling recrystallised from hot water. It proved to be readily soluble in hot water, more sparingly soluble in cold water, and crystallised in long obliquely terminated prisms which contained one molecule of water. The salt is permanent in the air or over sulphuric acid, but loses its water readily at 100° .

I. 0.6092 gram of the air-dried salt gave 0.3180 gram BaSO_4 .

II. 1.3540 gram of the air-dried salt lost at 100° 0.0576 gram H_2O .

	Calculated for $\text{Ba}(\text{C}_5\text{H}_2\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$.	Found.	
		I.	II.
Ba	30.72	30.69	...
H_2O	4.04	...	4.25

0.4749 gram of the salt dried at 100° gave 0.2587 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_5\text{H}_2\text{ClO}_3)_2$.	Found.
Ba	32.01	32.03

The solubility of the salt in cold water was determined in the usual way.

I. 10.2683 grams solution saturated at 19.1° gave 0.1149 gram BaSO_4 .

II. 6.8737 grams solution saturated at 19.1° gave 0.0747 gram BaSO_4 .

According to these determinations, the aqueous solution saturated at 19.1° contained the following percentages of the anhydrous salt:

I.	II.
2.06	2.00

Calcic β -chlorpyromucate, $\text{Ca}(\text{C}_5\text{H}_2\text{ClO}_3)_2 \cdot 3\text{H}_2\text{O}$.—This salt was prepared by neutralising with calcic carbonate a boiling solution of the acid. If the solution thus obtained is evaporated upon the water-bath, clustered, pointed prisms of an anhydrous salt are formed when the solution becomes highly concentrated. By evaporation *in vacuo* over sulphuric acid at ordinary temperatures, tufts of fine branching prisms are obtained which contain three molecules of water. The latter salt is permanent in the air, effloresces over sulphuric acid, and loses its water readily at 105° .

I. 0.4226 gram of the air-dried salt gave 0.1490 gram CaSO_4 .

II. 1.3627 gram of the air-dried salt lost at 105° 0.1902 gram H_2O .

	Calculated for $\text{Ca}(\text{C}_5\text{H}_2\text{ClO}_3)_2 \cdot 3\text{H}_2\text{O}$.	I.	Found.	II.
Ca	10.39	10.37
H_2O	14.03	13.95

0.5160 gram of the salt dried at 105° gave 0.2111 gram CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_5\text{H}_2\text{ClO}_3)_2$.	Found.
Ca	12.09	12.03

The pointed prisms obtained by evaporating the solution at 100° gave the following results:

0.4433 gram of the air-dried salt gave 0.1796 gram CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_5\text{H}_2\text{ClO}_3)_2$.	Found.
Ca	12.09	11.92

The solubility of the calcium salt in cold water was determined in the usual manner. The calcium was precipitated as oxalate, and converted into the sulphate before weighing.

I. 5.0960 grams solution saturated at 19.5° gave 0.0653 gram CaSO_4 .

II. 5.8981 grams solution saturated at 19.5° gave 0.0752 gram CaSO_4 .

According to these determinations, the aqueous solution saturated at 19.5° contained the following percentages of the anhydrous salt:

I.	II.
3.12	3.10

Ethyl β -chlorpyromucate, $C_5H_2ClO_3 \cdot C_2H_5$.—The ethyl ether was prepared by heating at 100° for four hours a mixture of 2 parts of the acid, 3 parts of absolute alcohol, and 2 parts of sulphuric acid (sp. gr. 1.84). On dilution with water, the ether separated as an oil, which was thoroughly washed and dried over calcic chloride. It then distilled without essential decomposition at 217° (mercury column completely in vapor) under a pressure of 764 mm. The liquid distillate solidified on cooling, with the formation of concentrically grouped prisms, which, after repeated recrystallisation by cooling the melted ether, showed the constant melting point of 29° – 30° .

0.1864 gram of substance gave 0.1523 gram AgCl.

	Calculated for $C_5H_2ClO_3 \cdot C_2H_5$.	Found.
Cl	20.34	20.19

Action of Nitric Acid.

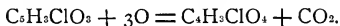
β -Chlorpyromucic acid is readily attacked by dilute nitric acid, but the oxidation is not smoothly effected, and the yield of chlorfumaric acid is comparatively small. The best results were obtained when the acid was boiled with 2 parts of nitric acid (sp. gr. 1.42) diluted with 5 parts of water. After the lapse of two hours, the action appeared to be completed, although a few drops of oil were still suspended in the clear solution. The products of the reaction were then extracted from the diluted solution with ether, the residue obtained by the evaporation of the ether pressed thoroughly with filter-paper and dried at 100° . The dry residue was then repeatedly washed with benzol, in which chlorfumaric acid is but sparingly soluble. The product thus obtained was readily soluble in water, almost insoluble in benzol, melted at 188° , and contained the percentage of chlorine required by chlorfumaric acid.¹

0.1089 gram substance dried over H_2SO_4 gave 0.1027 gram AgCl

¹ Kauder (J. prakt. Chem. [2] 31, 28) gives the melting point of chlorfumaric acid as 191° .

	Calculated for $C_4H_3ClO_4$.	Found.
Cl	23.59	23.31

The reaction may therefore be represented, in part at least, by the equation



Action of Bromine and Water.

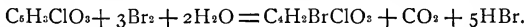
Since β -brompyromucic acid in aqueous solution is readily converted by an excess of bromine into mucobromic acid,¹ it seemed to us of interest to study the behavior of the β -chlorpyromucic acid under the same conditions, since a product containing bromine and chlorine might then be formed. The acid was therefore suspended in five times its weight of water, and an excess of bromine at once added. After heating for a short time, a clear nearly colorless solution was obtained, which was concentrated by evaporation on the water-bath. On cooling, the solution deposited a crystalline acid which was readily soluble in hot water or hot benzol, and but sparingly soluble in these solvents in the cold. The acid recrystallised from water formed thin rhombic plates which melted at 120° – 121° , but this melting point could easily be raised to 121° – 122° by recrystallisation from benzol.

An analysis of the substance dried over sulphuric acid showed that it was the mucochlorbromic acid whose formation we had been led to expect.

0.2871 gram substance gave 0.4486 gram $AgCl + AgBr$.

	Calculated for $C_4H_2BrClO_3$.	Found.
Br + Cl	54.11	54.45

The reaction was then precisely analogous to that by means of which mucobromic acid was formed from β -brompyromucic acid:



With the material which for the moment was at our disposal, we were unable to study the decomposition of the mucochlorbromic acid by alkalies. We shall hope in the future to prepare in this way a chlorbromacrylic acid, and compare it with the acid of the same composition already described by Mabery and Lloyd.²

¹ Proc. Am. Acad. **21**, 152.

² This Journal **3**, 127; and Proc. Am. Acad. **16**, 238.

$\beta\gamma$ -DICHLORPYROMUCIC ACID.

Hill and Sanger¹ had shown that in the decomposition of pyromucic tetrabromide or of ethyl pyromucic tetrabromide by alcoholic sodic hydrate, two isomeric dibrompyromucic acids are formed in not widely unequal quantities. There was, therefore, every reason to expect that two isomeric dichlorpyromucic acids could be found in the product formed in a similar way from ethyl pyromucic tetrachloride. Since we had found that a low temperature was essential to the preparation of a pure product, we allowed the ethyl pyromucate to absorb chlorine at 0° until a constant weight was reached, expelled the excess of chlorine by a current of dry air, and decomposed the product at once with an excess of an alcoholic solution of sodic hydrate. The best results were obtained when the tetrachloride was slowly added to a concentrated sodic hydrate solution, taking care to keep the mixture cold.

The sodium salts formed are sparingly soluble in alcohol, and after a short time can be removed by filtration. The alcoholic solution was freed from the excess of sodic hydrate by means of carbonic dioxide, and, after removing the sodic carbonate by filtration, distilled. The sodium salts left on distillation appeared to be identical with those already obtained and were therefore added to the main portion. The alcoholic distillate grew turbid when mixed with water, and gradually deposited a small quantity of a colorless oil which had a peculiar aromatic odor. The quantity of this oil was so small that no investigation of it has as yet been made.

The sodium salt which was obtained from the tetrachloride was dried, dissolved in hot water, and acidified with hydrochloric acid. In this way an acid was obtained which crystallised in finely felted needles, which usually melt at 155°. After two recrystallisations from benzol the acid melted at 168°–169°, and further recrystallisations failed to raise this melting point. Analysis showed this acid to be a dichlorpyromucic acid.

I. 0.4235 gram substance gave 0.5135 gram CO₂ and 0.0455 gram H₂O.

II. 0.2332 gram substance gave 0.3695 gram AgCl.

III. 0.2195 gram substance gave 0.3490 gram AgCl.

	Calculated for C ₅ H ₃ Cl ₂ O ₅ .	I.	Found. II.	III.
C	33.15	33.07
H	1.10	1.19
Cl	39.22	...	39.16	39.31

¹ Proc. Am. Acad. 21, 156.

The acid, which proved on subsequent investigation to be the $\beta\gamma$ -dichlorpyromucic acid, is sparingly soluble in cold water, readily in hot, and crystallises as the solution cools in finely felted needles. It is readily soluble in alcohol, ether, or in hot benzol; in cold benzol it is sparingly soluble and crystallises from it in short prisms. In hot chloroform it is also readily soluble, sparingly soluble in the cold. The ready purification of this acid by recrystallisation rendered it improbable that any sensible amount of an isomeric acid was formed with it. The most patient search has failed to show the formation of such a product in appreciable quantity, and from pure ethyl pyromucic tetrachloride almost pure $\beta\gamma$ -dichlorpyromucic acid is obtained at once. The yield of pure acid ordinarily obtained from pyromucic ether is not wholly satisfactory, since it amounts to about 50 per cent. of the weight of ether taken, or about 39 per cent. of the theoretical amount.

The solubility of the acid in cold water we determined as usual. A weighed quantity of a solution of the acid saturated at 19.5° was boiled with baric carbonate and the barium dissolved precipitated by sulphuric acid.

I. 36.2505 grams solution saturated at 19.5° gave 0.0619 gram BaSO_4 .

II. 35.6546 grams solution saturated at 19.5° gave 0.0615 gram BaSO_4 .

According to these determinations, the solution saturated at 19.5° contains the following percentages of acid:

I.	II.
0.27	0.27

Baric $\beta\gamma$ -dichlorpyromucate, $\text{Ba}(\text{C}_5\text{HCl}_2\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$.¹ — The barium salt may be most conveniently prepared by precipitating a

¹ We have already referred to the brief description of the $\beta\gamma$ -dichlorpyromucic acid published by Denaro in the *Gazzetta Chimica* (16, 333), and have asserted that the analyses of the two salts which he describes are not worthy of confidence. In support of our assertion we append his results in full, together with the analytical data upon which they depend. The errors in the calculated percentages are corrected in parenthesis.

Barium salt:

0.4480 gram of the salt lost at 110° 0.00204 gram H_2O .

	Calculated for $\text{Ba}(\text{C}_5\text{HCl}_2\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$.	Found.
H_2O	9.80	8.30 (0.445)

0.1939 gram of the dry salt gave 0.0769 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_5\text{HCl}_2\text{O}_3)_2$.	Found.
Ba	23.54 (27.56)	23.32

solution of the ammonium salt with baric chloride. It is rather sparingly soluble even in hot water, and still less soluble in cold water. It separates from a hot concentrated solution in fine clustered needles which contain three molecules of water. The crystals are permanent in the air, but lose their water readily at 100° .

I. 1.2048 gram air-dried salt lost at 100° 0.1170 gram H_2O .

II. 1.2118 gram air-dried salt lost at 100° 0.1132 gram H_2O .

III. 0.5694 gram air-dried salt gave 0.2393 gram BaSO_4 .

IV. 0.3783 gram air-dried salt gave 0.1593 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_5\text{HCl}_2\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$.	I.	II.	Found.	III.	IV.
H_2O	9.80	9.71	9.34
Ba	24.86	24.71	24.76	

I. 0.4828 gram salt dried at 100° gave 0.2250 gram BaSO_4 .

II. 0.5540 gram salt dried at 100° gave 0.2579 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_5\text{HCl}_2\text{O}_3)_2$.	I.	II.
Ba	27.56	27.40	27.36

The solubility of the salt in water at 19.5° was determined according to the method of V. Meyer.

I. 23.0222 grams solution saturated at 19.5° gave 0.0503 gram BaSO_4 .

II. 22.4890 grams solution saturated at 19.5° gave 0.0487 gram BaSO_4 .

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt :

I.	II.
0.46	0.46

Calcic $\beta\gamma$ -dichloropyromucate, $\text{Ca}(\text{C}_5\text{HCl}_2\text{O}_3)_2 \cdot 4\text{H}_2\text{O}$.—The calcium salt was prepared by boiling a solution of the acid with an

Calcium salt :

0.6942 gram of the salt lost at 110° 0.0300 gram H_2O .

	Calculated for $\text{Ca}(\text{C}_5\text{HCl}_2\text{O}_3)_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$.	Found.
H_2O	13.60	14.45 (4.32)

0.3024 gram of the salt gave 0.1072 gram CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_5\text{HCl}_2\text{O}_3)_2$.	Found.
Ca	10.00	10.42

These results can hardly be explained unless it is assumed that they contain both typographical and arithmetical errors. The two remaining analyses contained in Denaro's paper, two chlorine determinations in the free acid, are correctly calculated and agree well with the theory.

excess of calcic carbonate. It is readily soluble in hot water, less soluble in cold, and crystallises from a hot concentrated solution in long clustered needles which contain four molecules of water.

The crystallised salt is permanent in the air, effloresces slowly over sulphuric acid, and loses all its water readily at 110° .

I. 2.7640 grams air-dried salt lost at 110° 0.4160 gram H_2O .

II. 3.1275 grams air-dried salt lost at 113° 0.4707 gram H_2O .

	Calculated for $Ca(C_6HCl_2O_3)_2 \cdot 4H_2O$.	I.	Found.	II.
H_2O	15.26	15.05		15.05

I. 0.6595 gram salt dried at 110° gave 0.2227 gram $CaSO_4$.

II. 0.7004 gram salt dried at 113° gave 0.2366 gram $CaSO_4$.

	Calculated for $Ca(C_6HCl_2O_3)_2$.	I.	Found.	II.
Ca	10.00	9.93		9.94

The solubility of the salt in water at 19.5° was determined as usual. The calcium was precipitated as oxalate and the oxalate ignited with sulphuric acid.

I. 22.8797 grams solution saturated at 19.5° gave 0.0944 gram $CaSO_4$.

II. 21.5915 grams solution saturated at 19.5° gave 0.0891 gram $CaSO_4$.

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt:

I.	II.
1.21	1.21

Potassic $\beta\gamma$ -dichlorpyromucate, $KC_6HCl_2O_3$.—The potassium salt is readily soluble in hot water, but rather sparingly soluble in cold water, and separates from a hot concentrated solution in small prisms which are anhydrous.

I. 0.6130 gram substance dried at 120° gave 0.2435 gram K_2SO_4 .

II. 0.8200 gram substance dried at 120° gave 0.3265 gram K_2SO_4 .

	Calculated for $KC_6HCl_2O_3$.	I.	Found.	II.
K	17.84	17.83		17.87

Argentio $\beta\gamma$ -dichlorpyromucate, $AgC_6HCl_2O_3$.—If argentic nitrate is added to a cold aqueous solution of the acid, the silver salt is precipitated in the form of fine needles. For analysis we

prepared the salt by precipitating a dilute neutral solution of the ammonium salt with argentic nitrate, and recrystallising the precipitated salt from hot water. It is sparingly soluble even in hot water, and separates on cooling the hot saturated solution in fine needles.

I. 0.3230 gram substance dried over H_2SO_4 gave 0.1612 gram AgCl .

II. 0.2580 gram substance dried over H_2SO_4 gave 0.1282 gram AgCl .

	Calculated for $\text{AgC}_5\text{HCl}_2\text{O}_3$.	I.	Found.	II.
Ag	37.50	37.57		37.41

Ethyl $\beta\gamma$ -dichlorpyromucate, $\text{C}_5\text{HCl}_2\text{O}_3\text{C}_2\text{H}_5$.—The ethyl ether was prepared by heating at 100° for three hours a mixture of five parts of acid, eight parts of absolute alcohol, and five parts of concentrated sulphuric acid (sp. gr. 1.84). It was precipitated with water, washed with dilute sodic carbonate, and then with water. It is readily soluble in hot alcohol, more sparingly in cold, and crystallises in large needles which melt at 63° – 64° .

I. 0.2645 gram substance dried over H_2SO_4 gave 0.3640 gram AgCl .

II. 0.1933 gram substance dried over H_2SO_4 gave 0.2673 gram AgCl .

	Calculated for $\text{C}_5\text{HCl}_2\text{O}_3\text{C}_2\text{H}_5$.	I.	Found.	II.
Cl	33.98	34.02		34.18

$\beta\gamma$ -Dichlorpyromucamide, $\text{C}_5\text{HCl}_2\text{O}_2\text{NH}_2$.—The ethyl ether of $\beta\gamma$ -dichlorpyromucic acid is readily attacked by strong aqueous ammonia even in the cold, and in a short time is converted into the amide. The amide is sparingly soluble even in hot water, and crystallises in long slender needles which melt at 176° – 177° .

0.4015 gram substance dried over H_2SO_4 gave 28.5 cc. moist N at 23° under a pressure of 767 mm.

	Calculated for $\text{C}_5\text{HCl}_2\text{O}_2\text{NH}_2$.	Found.
N	7.78	8.03

The formation of but one dichlorpyromucic acid in the decomposition of the ethyl pyromucic tetrachloride by alkalies, while two isomeric acids are always obtained under the same circumstances from the corresponding bromine compound, made it impossible to predict its constitution from the method of formation. Still, its

comparatively high melting point, its physical properties, and the ready solubility of its calcium salt, in which it closely resembles the $\beta\gamma$ -dibrompyromucic acid, gave fair ground for the conjecture that it had a similar structure. A study of its oxidation products showed that such was the case, since we easily obtained from it mucochloric and dichlormaleic acids.

Action of Bromine and Water.

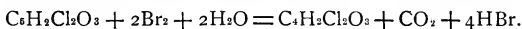
If bromine is added to $\beta\gamma$ -dichlorpyromucic acid suspended in six or eight times its weight of cold water, oxidation rapidly ensues, with the escape of carbonic dioxide. A slight excess of bromine was added, and the reaction completed by the aid of heat. On cooling, the solution solidified with the separation of colorless crystals, which when recrystallised from water and finally from benzol melted at 124° – 125° , and had the characteristic form of mucochloric acid. Analysis also gave the proper percentage of chlorine.

I. 0.2015 gram substance dried over H_2SO_4 gave 0.3408 gram AgCl .

II. 0.2320 gram substance dried over H_2SO_4 gave 0.3922 gram AgCl .

	Calculated for $\text{C}_4\text{H}_2\text{Cl}_2\text{O}_3$.	I.	Found.	II.
Cl	42.01	41.81		41.79

In this case the reaction may be represented by the equation



Action of Nitric Acid.

Nitric acid acts but slowly upon the $\beta\gamma$ -dichlorpyromucic acid, and for its complete oxidation we have found it necessary to take for one part of the acid 3 parts of concentrated nitric acid (sp. gr. 1.42) diluted with twice its weight of water. After boiling for five hours the action appeared to be complete, and as the clear solution deposited nothing on cooling, we extracted it with ether. The ether left upon evaporation a colorless crystalline mass, which proved to be a mixture of two substances, one readily soluble, the other but sparingly soluble in cold water. The sparingly soluble substance, when recrystallised from hot water, was recognised by its crystalline form and by its melting point, 124° – 125° , as mucochloric acid. The acid, which was readily soluble in cold water,

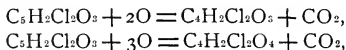
was neutralised with baric carbonate, the barium salt precipitated from its aqueous solution by alcohol, and the acid liberated from this purified barium salt again extracted with ether. The crystalline acid left by the evaporation of the ether was then dissolved in a small amount of water, and on standing, well formed rhombic plates separated, which were dried over sulphuric acid for analysis.

0.2233 gram substance gave 0.3433 gram AgCl.

	Calculated for $C_4H_2Cl_2O_4$.	Found.
Cl	38.38	38.01

The identity of this acid with dichlormaleic acid was further determined by the melting point of the anhydride prepared by sublimation, which we found to be 119° – 120° , in agreement with the statement of Ciamician and Silber.¹

The oxidation therefore took place in accordance with the following reactions,



and the dichlorpyromucic acid in question is thus conclusively shown to have its chlorine atoms in the β and γ positions.

PREPARATION OF ISOMERIC DICHLORPYROMUCIC ACIDS.

Although we had been unable to find the $\beta\delta$ -dichlorpyromucic acid among the products formed by the action of alkalies upon ethyl pyromucic tetrachloride, it seemed to us probable that it might be formed under the proper conditions by the direct action of chlorine upon ethyl pyromucate, or by the decomposition of its tetrachloride by heat alone.

Tönnies² had already shown that δ -brompyromucic acid could be formed by heating pyromucic tetrabromide, and Hill and Sanger³ had further shown that δ -brompyromucic acid and $\beta\delta$ -dibrompyromucic acid could conveniently be made by the action of bromine upon pyromucic acid at high temperature. As subsequent experiments in this laboratory had shown that these two acids could more advantageously be made by substituting the ethyl ether for the acid, and our own experiments had shown that the δ -chlorpyromucic acid could readily be made in this way, we proceeded to study the action of chlorine upon ethyl pyromucate

¹ Ber. d. chem. Ges. 16, 2396.

² Ibid. 11, 1038.

³ Proc. Am. Acad. 21, 135, 160.

at high temperature. It seems hardly necessary to describe in detail the numerous experiments which we made under widely varying conditions, each one of which yielded us purely negative results. Ethyl pyromucate was treated with chlorine at temperatures ranging from 145° to its boiling point, both by itself and after the addition of iodine or aluminic chloride, but in no case was the desired product obtained. Pyromucic acid and δ -chlorpyromucic acid also failed to give such a product when treated at high temperatures with chlorine, and we were equally unsuccessful when we used the chloranhydrides of these acids either with or without an excess of phosphoric pentachloride. We then studied the action of heat upon the tetrachloride of pyromucic acid itself, of its chloranhydride and ethyl ether, and of the ethyl ether of δ -chlorpyromucic acid, and found in each case that small quantities of a dichlorpyromucic acid were formed which closely resembled the $\beta\delta$ -dibrompyromucic. A more careful investigation further proved that in the decomposition of the ethyl pyromucic tetrachloride a second new dichlorpyromucic acid was formed concerning whose constitution we are not yet able to speak definitely. This acid we propose to call the χ -dichlorpyromucic acid until its structure is established. The amount of the dichlorpyromucic acids which we have been able to obtain is but small, and we have made many unsuccessful attempts to increase the yield by varying the temperature or the mode of heating, or by adding iodine, or aluminic or ferric chloride, before heating.

We first obtained the $\beta\delta$ -dichlorpyromucic acid by distilling under ordinary pressure the product formed by treating pyromucic acid with chlorine at 100° . Hydrochloric acid is given off in quantity, and, although a large carbonaceous residue is left in the retort, a liquid distillate is obtained which, after repeated distillation through a Hempel's column, amounts to about 85 per cent. of the weight of the pyromucic acid taken and then distills, leaving but an insignificant carbonaceous residue. This distillate is extremely complex in its nature, and we have as yet made no thorough study of its constituents. We found, however, that the portions which boiled between 196° and 220° gave considerable quantities of $\beta\delta$ -dichlorpyromucic acid when treated with cold water. They therefore contained the corresponding chloranhydride of the acid. The yield thus obtained amounted to but about 4 per cent. of the pyromucic acid taken. From ethyl pyromucic

tetrachloride we succeeded in obtaining a somewhat better yield. We found it advantageous to purify the tetrachloride by one distillation *in vacuo*, and to distill the product thus obtained under ordinary pressure. More or less carbonisation ensued, and on fractional distillation *in vacuo* through a Hempel's column¹ the distillate was found to contain considerable unaltered tetrachloride. That portion which boiled above 140° under 16 mm. pressure was therefore redistilled under ordinary pressure and the distillate again fractioned *in vacuo*. After repeated distillations we found that the portion which boiled between 118° and 123° under 16 mm. pressure partially solidified on cooling, and that a few crystals were also formed in the next lower fraction. These fractions were therefore strongly cooled and the crystalline solid removed by filtration and the liquid portions further distilled. The solid thus obtained proved to be the ethyl ether of the new χ -dichlorpyromucic acid melting at 197° – 198° , which we shall presently describe. When no more of this crystalline ether could be obtained by cooling, the liquid fractions were saponified by alcoholic sodic hydrate, the acids liberated by hydrochloric acid and separated through their calcium and barium salts. From the fraction boiling below 110° (16 mm.) we obtained chiefly δ -chlorpyromucic acid melting at 176° – 177° , although it yielded also a small quantity of $\beta\delta$ -dichlorpyromucic acid, which was readily isolated by means of its sparingly soluble barium salt. The fractions 110° – 118° and 118° – 123° apparently consisted chiefly of the ethyl ether of $\beta\delta$ -dichlorpyromucic acid, but the latter necessarily contained also a small amount of the crystalline ethyl χ -dichlorpyromucate held in solution. The two dichlorpyromucic acids could readily be separated through the different solubilities of their calcium salts, the calcic $\beta\delta$ -dichlorpyromucate like the calcium salt of the corresponding bromine derivative being very

¹ For fractional distillation under diminished pressure we used the extremely convenient apparatus of Anschütz. We found that the ease of separation could be materially increased by filling a few inches of the stem of the distilling flask with glass beads, and thus combining the Hempel's column with the vacuum distillation. The beads were supported upon a perforated disk of platinum foil slipped over the capillary air tube and held in place by a slight enlargement of the tube. The thermometer was then raised to the proper line by a short bit of small glass tubing dropped into the air tube. Hantzsch (Ann. Chem. (Liebig) 249, 57) has used with advantage for distillation under ordinary pressure a long necked boiling flask whose stem is partially filled with beads supported upon a platinum foil forced into the neck. We have for a long time used such a Hempel's column, but have supported the beads conveniently upon a glass bulb which nearly fills the stem and whose sealed neck is long enough to rest upon the bottom of the flask.

sparingly soluble in water. From 123° – 130° but an insignificant fraction was collected, and the fraction 130° – 153° consisted in part at least of unaltered ethyl pyromucic tetrachloride, from which $\beta\gamma$ -dichlorpyromucic acid was obtained.

100 grams of ethyl pyromucate yielded us 197 grams of the tetrachloride, and from this we obtained the following weights of pure products:

- 5.0 grams δ -chlorpyromucic acid.
- 12.2 grams $\beta\gamma$ -dichlorpyromucic acid.
- 2.7 grams χ -dichlorpyromucic acid.
- 16.1 grams ethyl χ -dichlorpyromucate.

If pyromucyl chloride is treated with chlorine at 0° , the chlorine is absorbed very slowly, but the gain in weight finally approximately corresponds with that required for the formation of a tetrachloride. If the tetrachloride is distilled under ordinary pressure, only an inconsiderable carbonaceous residue is left in the retort, and after repeated distillations through a Hempel's column under ordinary pressure a product is obtained which, when treated with water, yields the $\beta\delta$ -dichlorpyromucic acid and the χ -dichlorpyromucic acid. While the yield of the $\beta\delta$ -dichlorpyromucic acid thus obtained is somewhat greater than that obtained from the ethyl pyromucic tetrachloride, the yield of the χ -dichlorpyromucic acid is much smaller.

By treating ethyl δ -chlorpyromucate in the cold with chlorine, and distilling the addition product thus formed under ordinary pressure, we also obtained the $\beta\delta$ -dichlorpyromucic acid. While the yield was somewhat larger than that obtained from the ethyl pyromucic tetrachloride, it did not repay us for the loss of time and material involved in making the δ -chlorpyromucic acid. Moreover, to our surprise, we could obtain in this way none of the crystalline ethyl χ -dichlorpyromucate.

$\beta\delta$ -DICHLORPYROMUCIC ACID.

The acid whose preparation has just been described can most readily be purified by repeated precipitation from ammoniacal solution with calcic chloride, and recrystallisation from chloroform. The acid thus purified gave on analysis the following results:

I. 0.2577 gram substance gave 0.3129 gram CO_2 and 0.0259 gram H_2O .

II. 0.1933 gram substance gave 0.3053 gram AgCl .

	Calculated for $C_6H_2ClO_3$.	Found.	
		I.	II.
C	33.15	33.11	...
H	1.10	1.12	...
Cl	39.22	...	39.04

$\beta\delta$ -Dichloropyromucic acid is readily soluble in ether or alcohol. It dissolves readily in hot water, benzol, or chloroform, and the greater part of the acid is in each case deposited on cooling in oblique prisms, which are frequently twinned in forms which can hardly be distinguished from those of the $\beta\delta$ -dibromopyromucic acid. The acid melts sharply at 155° – 156° , and sublimes unaltered at a higher temperature.

The solubility of the acid in water at 19.5° was determined in the usual manner. A weighed quantity of a solution of the acid saturated at 19.5° was boiled with baric carbonate, and the barium dissolved determined by precipitation with sulphuric acid.

I. 42.8007 grams solution saturated at 19.5° gave 0.0724 gram $BaSO_4$.

II. 51.4109 grams solution saturated at 19.5° gave 0.0907 gram $BaSO_4$.

According to these determinations, the solution saturated at 19.5° contained the following percentages of acid :

I.	II.
0.26	0.27

Baric $\beta\delta$ -dichloropyromucate, $Ba(C_6HCl_2O_3)_{2.4}H_2O$.—The barium salt was prepared by precipitating a dilute solution of the ammonium salt with baric chloride, and recrystallising the product thus obtained from water. The salt is sparingly soluble in hot water, still less soluble in cold water, and crystallises from a hot concentrated solution in long irregular flat prisms which contain four molecules of water.

The salt is permanent in the air, effloresces over sulphuric acid, and loses its water readily at 100° .

I. 1.4513 gram air-dried salt lost at 100° 0.1795 gram H_2O .

II. 0.4908 gram air-dried salt gave 0.1981 gram $BaSO_4$.

	Calculated for $Ba(C_6HCl_2O_3)_{2.4}H_2O$.	Found.	
		I.	II.
H_2O	12.66	12.37	...
Ba	24.07	...	23.73

0.4751 gram salt dried at 100° gave 0.2205 gram $BaSO_4$.

	Calculated for $\text{Ba}(\text{C}_5\text{HCl}_2\text{O}_3)_2$.	Found.
Ba	27.56	27.29

The solubility of the salt in water at 19.5° was determined in the usual manner.

I. 28.4671 grams solution saturated at 19.5° gave 0.0561 gram BaSO_4 .

II. 28.6844 grams solution saturated at 19.5° gave 0.0573 gram BaSO_4 .

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt :

I.	II.
0.42	0.43

Calcic β -dichlorpyromucate, $\text{Ca}(\text{C}_5\text{HCl}_2\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$.—The calcium salt was prepared by precipitating a dilute solution of the ammonium salt with calcic chloride, and recrystallising the product from hot water. It is but sparingly soluble in hot water, still less soluble in cold water, and separates from a hot concentrated solution in flattened prisms with rectangular terminations. The crystallised salt is permanent in the air, effloresces slowly over sulphuric acid and loses all its water at 125° .

I. 1.5490 gram air-dried salt lost at 125° 0.1820 gram H_2O .

II. 0.4067 gram air-dried salt gave 0.1219 gram CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_5\text{HCl}_2\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$.	I.	Found.	II.
H_2O	11.90	11.75
Ca	8.81	...	8.81	...

0.6899 gram salt dried at 125° gave 0.2332 gram CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_5\text{HCl}_2\text{O}_3)_2$.	Found.
Ca	10.00	9.94

The solubility of the salt in water at 19.5° was determined in the usual manner. The calcium was precipitated as oxalate and ignited with sulphuric acid.

I. 32.1733 grams solution saturated at 19.5° gave 0.0244 gram CaSO_4 .

II. 36.7555 grams solution saturated at 19.5° gave 0.0289 gram CaSO_4 .

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt :

I.	II.
0.22	0.23

Ethyl $\beta\delta$ -dichlorpyromucate, $C_8HCl_2O_3C_2H_5$.—The ethyl ether was prepared by the action of ethyl iodide on the silver salt, and is a heavy liquid of pleasant odor. It melts at 2° – 3° , and distills at 116° – 118° under a pressure of 16 mm., the oil-bath being at 165° – 175° . An analysis of the distilled ether gave the following result:

0.2157 gram substance gave 0.2957 gram AgCl.

	Calculated for $C_8HCl_2O_3C_2H_5$.	Found.
Cl	33.98	33.89

$\beta\delta$ -Dichlorpyromucamide, $C_8HCl_2O_2NH_2$.—The ethyl ether is but slowly attacked by concentrated ammonia in the cold, but at 100° it is readily converted to the amide. The amide is sparingly soluble in cold water, more readily in hot, and separates from a hot concentrated solution in long needles, which on standing are converted into oblique prisms which melt at 153° – 154° .

0.2781 gram substance dried over H_2SO_4 gave 20.0 cc. moist N at 25.5° under a pressure of 766 mm.

	Calculated for $C_8HCl_2O_2NH_2$.	Found.
N	7.78	8.06

Although the melting point, the crystalline form, and the insolubility of its calcium salt showed that this acid closely resembled the $\beta\delta$ -dibrompyromucic acid, it was evidently necessary to establish the position of the chlorine atoms by means of its oxidation products.

Action of Bromine and Water.

Hill and Sanger¹ found that the $\beta\delta$ -dibrompyromucic acid was readily attacked by aqueous bromine in the cold with the formation of monobrommaleyl bromide. The $\beta\delta$ -dichlorpyromucic acid is but slowly attacked by aqueous bromine in the cold, and we therefore suspended it in five times its weight of water, added at once somewhat more than four atoms of bromine, heated until the oil which was first formed had almost all disappeared, and evaporated the solution at a gentle heat. The crystalline mass thus obtained was readily soluble even in cold water, and very sparingly soluble even in hot chloroform or benzol. The product was dissolved in cold water, filtered, and evaporated nearly to dryness.

¹ Proc. Am. Acad. 21, 165.

The crystals which separated were pressed dry with filter paper, washed carefully with hot benzol, and recrystallised from a little hot water. The acid thus prepared crystallised in microscopic crystals which melted at 189° – 190° ,¹ and proved on analysis to contain the percentage of chlorine required by monochlorofumaric acid.

0.1288 gram substance dried over H_2SO_4 gave 0.1227 gram AgCl.

	Calculated for $C_4H_3ClO_4$.	Found.
Cl	23.59	23.55

The oxidation with bromine and water therefore takes place in accordance with the following equation:



Since the $\beta\delta$ -dichloropyromucic is but slowly attacked even by concentrated nitric acid, it was not thought worth while to study the reaction in detail.

[To be continued.]

φ. 1. 2.

ON THE PRESENCE OF SUGAR-YIELDING INSOLUBLE² CARBOHYDRATES IN SEEDS.

BY W. MAXWELL.

In the physiological study of seeds and plants, and in the chemical analysis of their known constituents, anything like an even approximate determination of the sum and character of those constituents has not been made, research having been pursued within limits which have acknowledged a large percentage residue of "undetermined matter." These undetermined matters, excluding nitrogenous substances whose nature is not fully understood, have been summarily expressed as nitrogen-free extract matter (N-freie Extractstoffe).

It has not appeared probable that this large proportion of the total constituent matters of seeds is incapable of a chemically expressible composition, and without a definite function in the life

¹ Kauder (J. prakt. Chem. [2], **31**, 28) gives the melting point as 191° .

² Insoluble in water and diastase.

and development of the plant; and, further, that those matters can only act a negative part in the appropriation of vegetable substances by the animal system. These considerations have led to investigation.

In the course of researches conducted by Prof. E. Schulze and Dr. E. Steiger¹ with the seeds of *Lupinus luteus*, the non-nitrogenous matter of those seeds, after the separation and study of the soluble carbohydrates by Dr. Steiger,² was found to contain an insoluble carbohydrate which, by treatment with a dilute mineral acid, yielded a sugar capable of reducing Fehling's solution, and which exhibited all the properties of galactose. This insoluble sugar-yielding body was named Paragalactin, and has the formula of the soluble galactin, $C_6H_{10}O_5$.³

The author, during a study of the legumes *Pisum sativum*, *Faba vulgaris*, and *Vicia sativa*, at the instance of Prof. Schulze, and as a part of that special course of research of the Zürich Agricultural Chemical Laboratory, made an investigation of the non-nitrogenous insoluble residues in respect of the presence of sugar-yielding bodies in those seeds.

The method of research was as follows: About one kilo of finely ground material was saturated with ether, for the removal of the fats. The fat-free material was treated with dilute potassium hydrate in order to take out the greater part of the proteid bodies. Pouring off the alkaline extractant and washing with water until neutral, the material was further treated with a solution of diastase for the separation of the amyloids. Having by aid of these several processes removed from the original material the fats, albuminoids, starches, and, of course, all soluble carbohydrates, a residue was left which was composed of cellulose, the remnants of the less soluble albuminous matters, and that large aggregate already expressed as nitrogen-free extract matter. That insoluble residue was boiled with a solution of sulphuric acid of a concentration of 3.5 per cent. for one hour. After filtering, the extraction was diluted with an equal volume of water and further boiled for two hours under a condenser, and afterwards neutralised with barium carbonate and the neutral solution evaporated down to a syrup consistence. The syrup residue was extracted by boiling consecutively with alcohols of respectively 95 and 90 per cent. concentrations. The alcoholic extractions, after further

¹ Ber. d. chem. Gesell. 2, 1887.

² Inaugural dissertation, 1887.

³ Ibid.

various treatments to obtain those more pure, were set aside in desiccators for primary crystallisation, or evaporated down and the water solution of the residue studied direct.

As the results obtained in the general investigations show very considerable variations, the properties and data pertaining to each variety of seeds that has been studied will be separately given. This must more particularly be done because the researches, which were to be made with the varieties of legumes already specified, have been extended so as to include a study of other kinds, embracing also representatives of the monocotyledons.

Vicia sativa.

The final alcoholic extraction, obtained, as already described, by boiling the sulphuric acid hydration product of the original non-nitrogenous residue with alcohol, after standing for some eight days in the desiccator, was a half-crystallised, half-syrup mass, which the presence of non-crystallisable bodies made it very difficult to obtain in a pure state.

By adding a few drops of the syrup, or of the water solution of the same, to boiling Fehling's solution, a heavy precipitation of copper oxide occurred, indicating that a reducing sugar was present.

When heated with concentrated nitric acid, mucic acid was obtained as the product of oxidation, having a melting point of 209° – 210° C.

In order to observe the action of an aqueous solution of the body upon the ray of polarised light, the sugar contained in a given volume was determined by means of Fehling's solution.

100 cc. of the aqueous solution contained 6.48 per cent. sugar. The value of the rotatory action was calculated according to the formula $[\alpha]_D$.¹

$$[\alpha]_D = \frac{A \times 0.346 \times 100}{l \times P}$$

$$a = 22.1,$$

$$l = 2.0,$$

$$P = 6.48.$$

$$[\alpha]_D = \frac{22.1 \times 0.346 \times 100}{2 \times 6.48} = \frac{764.66}{12.96} = +59^{\circ}.$$

¹ Landolt.

If the polarisation value of the body be considered in relation with its reducing action upon Fehling's solution and the formation of mucic acid as an oxidation product, it is indicated that more than one sugar kind is contained in the solution. That galactose is present is proved by the fact that the body yields mucic acid when heated with concentrated nitric acid, that sugar being the only one of the glucoses which gives mucic acid as a product of oxidation. However, as the rotatory power of galactose is 81.5, it is apparent that at least one other sugar is present which operates upon the ray of polarised light to the left. The levo-rotatory influence, with the non-crystallisable property of a large part of the body, suggests the presence of levulan. At present it has not been determined.

Faba vulgaris.

With this variety a more developed crystallisation was obtained from the alcoholic extraction in a form resembling galactose, white crystals partially separating from the syrup upon the sides of the crystallising dish. However, a pure preparation of that sugar was not obtained on account of the considerable mass of attaching syrup.

The properties exhibited by the body were in part similar to those in the example of *Vicia sativa*.

Fehling's solution was powerfully reduced.

A large amount of mucic acid was obtained by heating the body with concentrated nitric acid, with a melting point of 208°–209° C.

The value of polarisation was + 78.3

In the example of *Faba vulgaris*, the reducing of a copper solution and the large yield of mucic acid by treatment of the body with nitric acid not only demonstrate the presence of galactose; the high reading of the rotatory action of the aqueous solution of the sugar indicates that the insoluble carbohydrate present in the non-nitrogenous matter of those seeds is, in most part, convertible into galactose.

Pisum sativum.

The alcoholic extraction did not stand to allow of the possibility of getting crystallised sugars; it was directly examined in respect of its properties.

The reducing of Fehling's solution and the yielding of mucic acid when heated with concentrated nitric acid were as characteristic as in the foregoing examples.

An aqueous solution of the syrup which contained 9.5 grams of sugar in 100 cc., according to the formula $[\alpha]_D$, showed a dextro-rotatory reading of $+80.0$.

It thus is indicated that the seeds of *Pisum sativum* contain an insoluble carbohydrate which, upon treatment with a dilute mineral acid, yields an inversion product which is wholly galactose. That insoluble carbohydrate *must be paragalactin*.

In addition to the investigation of those legumes, research was conducted with certain representatives of the monocotyledons, in order to observe if those insoluble carbohydrates were more generally distributed through vegetable organisms.

A portion of the cattle food prepared from the cocoa seed (*Palmacea*) was treated the same as the examples already given. The final alcoholic extraction which had been evaporated to a syrup, after standing some weeks in a desiccator, was a half-crystallised, half-syrup mass, and the crystallisation could not be further induced by treatments with alcohol in vacuum.

The syrup reduced Fehling's solution, and, upon treatment with concentrated nitric acid at a moderate heat, a large yield of mucic acid was given.

An aqueous solution of the body, containing 10.314 grams in 100 cc., gave a dextro-rotatory reading, according to the given formula, of $+81.0^\circ$. It appears that the given specimen of *Palmacea* contains the galactose-yielding carbohydrate present in *Pisum sativum*, which is indicated by the same optical and chemical properties. In one other representative of the *Palmacea*, the palm nut, the inversion product of the non-nitrogenous insoluble matter agreed chemically in its properties with the cocoa-nut. The action of its aqueous solution upon the ray of polarised light was very different; it gave a reading of $+29.8^\circ$.

The latter example shows the properties peculiar to the alcoholic extract obtained in the case of *Vicia sativa*. The presence of galactose in the non-crystallisable syrup was demonstrated by oxidising with nitric acid, which gave a formation of mucic acid. The low dextro-reading of the polariscope, however, indicates that a considerable proportion of some sugar is present, rotating the polarised ray to the left. That sugar may be levulose, which is indicated by the non-crystallisable property of the syrup and by its optical behavior. If levulose were the sugar present, it must be in a less proportion than the galactose, otherwise the dextro-

rotatory action of the latter body had been further neutralised by the comparatively greater negative operation of the levulose.

The researches were further extended to coffee berries and soja beans. The alcoholic syrup extracts obtained from the inverted non-nitrogenous residues of those seeds, in addition to exhibiting the chemical and optical properties peculiar to the previous examples treated of, yielded large crystallised preparations of galactose sugar. By recrystallising several times out of alcohol, chemically pure preparations were obtained. Aqueous solutions of the sugar were prepared, containing 10 grams in 100 cc., the sugar having been previously dried at 100° C. The solutions were brought into the observation tube at a temperature of 17° C.

The rotatory powers of the sugars obtained from the respective seeds were as follow :

$$\text{Soja beans} = +81.3$$

$$\text{Coffee berries} = +81.1$$

The rotatory values assigned to galactose prepared from milk sugar by the given authorities are :

$$\text{Meisel}^1 = +81.53,$$

$$\text{Scheibler}^2 = +81.2,$$

$$\text{Tollens}^3 = +81.40$$

Upon resuming the study of the legumes at the Harvard College Laboratory, the author investigated the seeds of *Phaseolus vulgaris*, and with a similar result in respect of the presence of at least one insoluble carbohydrate, which by treatment with dilute sulphuric acid was converted into galactose. Paragalactin appears thus to be present in the insoluble non-nitrogenous matters of the "Boston bean."

It having been demonstrated that the insoluble non-nitrogenous matters of certain seeds contain sugar-yielding bodies, and that those carbohydrates appear, in some representatives, to form almost the whole of the non-nitrogenous substance, excluding cellulose, it became desirable to obtain a quantitative estimation of the relative amounts of those carbohydrates contained in the respective varieties of the legumes under investigation.

To that end a method of estimation was adopted based upon the principle of the previous separation of the fats, soluble carbohydrates, starch, and the chief part of the albuminoids. The

¹ J. prakt. Chem. 22, 100.

² Ber. d. chem. Gesell. 17, 1731.

³ Ibid. 17, 678.

nitrogen still contained in the residue was determined and calculated as representing unremoved proteids. The proteids, with the cellulose and any remnant of mineral matter, were deducted from the amount of the residue, and the remainder was accepted, by difference, as expressing the percentage of insoluble carbohydrates.

A second and direct method of estimating approximately the amount of those bodies was by inversion of a given weight of the residue with hydrochloric acid, allowing, as by the previous method, for the sum of proteids and cellulose, and determining the sugar of the inversion product by means of Fehling's solution gravimetrically.

Estimations were made of the quantitative amounts of those bodies in the representatives of legumes already qualitatively treated of.

Pisum sativum.

The mean of two determinations showed that the nitrogen contained in residue, obtained according to the method described, was = 6.147 per cent. That amount, when multiplied by the nitrogen factor¹ of the albuminoids present in legumes, gives :

$$\begin{array}{rcl} 6.147 \times 5.75 & = & 35.34 \text{ per cent. proteids,} \\ & & 14.64 \text{ " cellulose.} \\ \hline & & 49.98 \text{ "} \end{array}$$

Amount of insoluble carbohydrates in the residue, 50.02 per cent. ; calculated from the original material, 20.02 per cent.

The result of the estimation of those bodies by direct inversion of the residue was as follows :

$$\begin{array}{l} 7.794 \text{ grs. res. (18.949 grs. orig. mat.)} = 3.888 \text{ grs. sugar,} \\ \phantom{7.794 \text{ grs. res. (18.949 grs. orig. mat.)}} = 3.499 \text{ grs. carbohydrate,} \\ \phantom{7.794 \text{ grs. res. (18.949 grs. orig. mat.)}} = 18.46 \text{ per cent.} \end{array}$$

Between the estimation by difference and by direct inversion a variation of only 1.5 per cent. occurred, indicating that practically the whole of the insoluble non-nitrogenous matters present in the seeds of *Pisum sativum* is convertible into a sugar which was previously seen to be galactose, the hydration product of paragalactin.

¹ Ritthausen; Die Eiweissstoffe der Getreidearten und Hülsenfrüchte.

Faba vulgaris.

The mean of two determinations of nitrogen present in the residue was 8.587 per cent.

$$\begin{array}{rcl} 8.587 \times 5.75 & = & 49.37 \text{ per cent. proteids,} \\ & & 16.79 \quad \text{"} \quad \text{cellulose.} \\ \hline & & 66.16 \quad \text{"} \end{array}$$

Insoluble carbohydrates in residue, 33.83 per cent. ; calculated from original material, 14.41 per cent.

Determination by direct inversion :

$$\begin{array}{l} 6.092 \text{ grs. res. (14.298 grs. orig. mat.)} = 1.083 \text{ grs. sugar,} \\ \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad = 0.975 \text{ gr. carbohydrate,} \\ \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad = 6.819 \text{ per cent.} \end{array}$$

In the example of *Faba vulgaris* only about one half of the residue matter, indicated by the "difference" method as being insoluble carbohydrate, was convertible into sugars. The remaining portion will be further investigated.

Vicia sativa.

Two nitrogen determinations gave a mean of 8.984 per cent.

$$\begin{array}{rcl} 8.984 \times 5.75 & = & 51.628 \text{ per cent. proteids,} \\ & & 11.182 \quad \text{"} \quad \text{cellulose.} \\ \hline & & 62.84 \quad \text{"} \end{array}$$

Insoluble carbohydrates in residue, 37.16 per cent. ; calculated from original material, 15.162 per cent.

Determination by direct inversion :

$$\begin{array}{l} 7.457 \text{ grs. res. (16.785 grs. orig. mat.)} = 1.372 \text{ grs. sugar,} \\ \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad = 1.234 \text{ grs. carbohydrate,} \\ \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad = 7.36 \text{ per cent.} \end{array}$$

Those quantitative data show a close resemblance to the results obtained in the example of *Faba vulgaris*.

Phaseolus vulgaris.

The mean of two nitrogen determinations was 3.425 per cent.

$$\begin{array}{rcl} 3.425 \times 5.75 & = & 19.693 \text{ per cent. proteids,} \\ & & 21.770 \quad \text{"} \quad \text{cellulose.} \\ \hline & & 41.463 \quad \text{"} \end{array}$$

Insoluble carbohydrate in residue, 58.537 per cent.; calculated as original material, 8.2 per cent.

Determination by direct inversion :

3.524 grs. res. (25.27 grs. orig. mat.) = 2.026 grs. sugar,
= 1.8 grs. carbohydrates,
= 7.12 per cent.

In recapitulating the results of the investigations and the data which have been obtained in relation to those examples of legumes and of other seed kinds that have been under consideration, it appears to have been established that the insoluble non-nitrogenous matters, exclusive of cellulose, contained in the seeds of certain vegetable species are carbohydrate bodies which, in great or less proportion, are convertible by treatment with a dilute mineral acid into sugars. It has also been observed that the sugar most constantly and abundantly yielded as the hydration product of those insoluble carbohydrates is galactose, indicating that the carbohydrate in most instances is paragalactin. Other carbohydrates appear to be contained in those seeds in addition to the galactose-yielding body, which has been shown by the optical and chemical properties of their inversion products. Further, the quantitative data obtained have enabled an approximately exact estimation to be made of the total sum of the nitrogen-free extract matters, and of the carbohydrate proportion of those matters which is directly convertible into sugars. In the example of *Pisum sativum* it was observed that one-fifth of the whole composition matter of the seed consisted of an insoluble carbohydrate which was almost wholly convertible into galactose. The nitrogen-free extract matter contained in the seeds of *Phaseolus vulgaris* did not amount to quite ten per cent. of the constituent substances; nearly the whole of that amount, however, as in the case of *Pisum sativum*, was convertible into galactose. The examples *Faba vulgaris* and *Vicia sativa* contained respectively about fourteen and fifteen per cent. of those non-nitrogenous bodies; but in those examples not more than one half of those amounts yielded to the action of the dilute mineral acid, giving sugar hydration products.

The main result achieved by these researches is the finding of a more intelligible and scientific expression for all that portion of the constituent matter of seeds hitherto practically considered as a non-nitrogenous, valueless residue, and indicating what may be

the function of those matters in the physiological economy of the plant. It also appears that those matters, constituting so large a part of seeds, may and do exercise a nutritive office in the animal system, which was also shown by the author in the artificial digestion studies of certain seeds.¹

The question of the locality of those insoluble carbohydrates in the organism of the seed was studied microscopically by Prof. Cramer, Zürich, at the instance of Prof. E. Schulze. It appears that those bodies are secreted in the cells of the endosperm, and must be considered as a reserve material of the seed, and as contributing to the support of the embryo during germination. Prof. Cramer found in the examples of the cocoa palm, coffee, soja, and of the legume seeds specified in the researches, that the thick membranes of the cells of the cotyledons resist the direct action of a solution of cuprammonia; after, however, those membranes have been heated for a time in a dilute solution of mineral acid, whereby paragalactin and other carbohydrates are separated out, the cellulose residue of the membranes is soluble in the cuprammonia solution. Those membranes, before treatment with the acid, were insensible to color reagents. After the removal of the insoluble carbohydrates the cellulose residue gave a vivid blue reaction when treated with a mixture of chloride iodide of zinc.

Chemically, those insoluble carbohydrates are distinguished from the soluble carbohydrates and starch by their insolubility in water and diastase. From cellulose, as it has been shown, the distinction occurs in the solubility of those bodies in dilute acids and their non-solubility in cuprammonia, which is the reagent in which cellulose most readily dissolves.

HARVARD COLLEGE LABORATORY.

¹ This Journal 11, No. 5.

REVIEWS AND REPORTS.

ON THE FORMATION OF OZONE, HYDROGEN PEROXIDE, AND NITROUS ACID AS PRODUCTS OF COMBUSTION, AND ON THEIR PRESENCE IN THE AIR.

It is hardly necessary to refer to the number of chemists who have already worked on this subject, or to commend the excellence of their work. The names of Schönbein, Houzeau, Schoene, Berthelot, and Traube will at once suggest themselves. It would seem, however, that they all worked under the same difficulty, the lack of proper reagents to distinguish accurately between the reactions of ozone, hydrogen superoxide, and nitrous acid. In recent numbers¹ of the *Bulletin de la Société chimique de Paris* there are six articles by Prof. L. Ilosvay de N. Ilosva, of the Polytechnic School at Buda-Pesth, which show very accurate and painstaking work, and, if the results obtained are reliable, will materially modify the ideas now held.

The first paper is on reactions of nitrous and nitric acids. The author finds in sulphanilic acid and naphthylamine a reagent which acts on nitrous acid, but not on hydrogen peroxide or ozone. This reaction was discovered by Griess,² who first studied the action of diazo-benzene-sulphonic acid on naphthylamine. He obtained his diazo-benzene-sulphonic acid by treating sulphanilic acid with nitrous acid, and calls attention to the extreme delicacy of the reaction, minute traces of nitrous acid sufficing to produce a dark red color in presence of dilute sulphuric acid. The colored substance formed is an amido-azo-derivative of the formula $C_6H_4(SO_3H)N=NC_{10}H_6NH_2$, called by Griess azo-amido-naphthalene-benzene-sulphonic acid.

Ilosvay increases the sensitiveness of the reaction by substituting acetic for sulphuric acid. He can detect nitrous acid in aqueous solution in a dilution of one part of nitrous acid to one thousand million parts of water, but finds that quantitative determinations of nitrous acid cannot be made by this reagent. To detect nitric acid in the presence of nitrous, he first breaks down the latter by Peccini's³ method with urea in the acidulated solution, and detects nitric acid by the blue color produced by diphenylamine and concentrated sulphuric acid. This is a fairly sensitive reaction, but its sensitiveness is limited to a dilution of $\frac{1}{95000}$, and it is caused by the oxidising agents as well as by nitric acid. For very dilute solutions it is better to reduce to nitrous acid and test by Griess's reaction. Granulated zinc in presence of alkali is the best reducing agent. In this way one part of nitric acid in two hundred and fifty million parts of water is easily detected.

¹ September and November, 1889.² Ber. d. chem. Gesell. **12**, 425; **15**, 2191.³ Ztschr. anal. Chem. 1880, 354.

The second paper is on the action of oxidising agents on azo-amido-napthalene-benzene-sulphonic acid, the coloring matter produced by Griess's reaction. Chlorine, dilute chromic acid, acidulated permanganate, and hydrogen peroxide turn this red substance orange yellow, the orange shade remaining when exposed to the air; and ozone turns the substance reddish yellow, changing on exposure to the air to a red shade, differing from the original red. These changes are supposed to be caused by the formation of oxy-azo compounds. From his experiments the author concludes that the amido-azo coloring substance can be used as a delicate reagent for ozone and hydrogen peroxide, and that nitrous acid can exist for a short time in the presence of ozone and hydrogen peroxide, because its oxidation is not immediate; but if enough ozone or hydrogen peroxide be present, it is quickly oxidised to nitric acid.

In the third paper, methods for preparing sodium hydroxide free from nitrous acid are described. This reagent is required for the following work, and is prepared either by decomposing water with sodium, or by reducing the nitrites contained in ordinary hydroxide with granulated zinc.

In the fourth article the author takes up the question of the formation of ozone, hydrogen peroxide, nitrous and nitric acids, as products of the active combustion of various substances and of the slow combustion of phosphorus. He reviews the literature and shows the divergence in the statements of the numerous chemists who have worked on this subject. He studies at length the various reagents, and commends as the best for ozone its odor, by which one can detect it in a dilution of $\frac{1}{1500000}$. The best chemical reagent is paper impregnated with thallium suboxide, which ozone turns brown, while hydrogen peroxide does not change it. It is true that nitrous acid turns it brown, but if the action continues, colorless thallium nitrate is formed. This is not as sensitive a test for ozone as its odor; the paper requires 20-25 minutes to turn brown with ozone in a dilution of $\frac{1}{1204000}$. The reagents commonly used to detect hydrogen peroxide are iodide of potassium and starch, chromic acid and ether, acidulated potassium permanganate, Wurster's¹ paper (impregnated with di- and tetra-methyl-phenylene-diamine), and titanium dioxide dissolved in concentrated sulphuric acid; the last mentioned is the only one not acted on by ozone or nitrous acid. Hydrogen peroxide turns it yellow. It is not very sensitive, but is a sure reagent to detect hydrogen peroxide in dilutions not exceeding $\frac{1}{90000}$.

It is to be noted that in a dilute solution hydrogen peroxide can exist in presence of an excess of ozone; but if it is in excess the ozone is destroyed. Hence both cannot be present unless ozone is in excess.

The author examined the products of combustion of hydrogen,

¹ Ber. d. chem. Gesell. 19, 3208.

carbon monoxide, methane, illuminating gas, benzene, alcohol, ether, petroleum, stearin candles, magnesium, zinc, iron filings, sulphur, and phosphorus.

He examined the gases escaping from stoves heated with wood and with coke, the air surrounding the voltaic arc, and the products formed by the slow combustion of phosphorus. To test for ozone, the flames of the burning substances were covered with a glass tube, the gaseous products of combustion collected and tested with all reagents used for ozone. Thallium suboxide was not changed, and only those reagents which act on nitrous acid as well as on ozone were changed. In examining the slow combustion of phosphorus, the flask containing the phosphorus was filled with water and connected with two Peligot tubes filled with water; then followed a Winkler's absorption apparatus containing the amido-azo compound, then a tube with thallium suboxide paper, then an absorption tube with potassium iodide and starch, and finally an aspirator. The water in the flask was replaced by pure air (leaving a little water in contact with the phosphorus), and the aspirator set in motion; in four minutes after the phosphorus came in contact with air, the amido-azo compound turned yellow, one minute later the thallium protoxide turned brown, twelve minutes later the starch paste was quite blue. The water in the Peligot tubes gave no reaction for hydrogen peroxide, but it was found in the water in contact with the phosphorus. In the slow combustion of phosphorus, then, both ozone and hydrogen peroxide are formed.

Ilosvay then took up the question of the formation of hydrogen peroxide as a product of active combustion. He repeated the experiments of Traube,¹ and confirms Traube's statements that carbon monoxide does not burn in perfectly dry air, but burns in moist air, and that if the surface of water is brought in contact with the carbon monoxide flame, or with the hydrogen flame, the water will be found to contain hydrogen peroxide. But Ilosvay found that if carbon monoxide or hydrogen is burned in moist air and the product mixed with a little water, hydrogen peroxide is sometimes present, sometimes not; he discovered that its formation depends on the flame coming in contact with the moisture condensed on the sides of the vessel; that if the flame is small and kept in the centre of the vessel, avoiding contact with the walls, no hydrogen peroxide is formed. These results led him to try whether all combustible gases and vapors when burned in contact with water form hydrogen peroxide. He burned carbon monoxide, hydrogen, methane, illuminating gas, alcohol, ether, petroleum, stearin candles, and benzene in a suitable apparatus, directing the flames into water. As a result, the water was found in every case to contain hydrogen peroxide after a minute or two.

Ilosvay says: "Considering that ozone is decomposed at 240° , and hydrogen peroxide at dull red heat, it is not supposable that

¹ Ber. d. chem. Ges. 18, 1891.

either could exist in a hot flame, and not surprising that hydrogen peroxide was only formed when the flame was cooled by contact with water."

He burned all the above-mentioned substances in air, and mixed the products of combustion with water, and in no case was the water found to contain hydrogen peroxide. He passed the products of combustion of fuel through water, and proved that no hydrogen peroxide was formed. Nitrous and nitric acids were always formed by quick combustion of the substances mentioned, and were best absorbed by dilute alkali (a 20 per cent. solution of pure sodium hydroxide). He attributes the formation of acids of nitrogen to the union of nitrogen and oxygen of the air, brought about by the heat of combustion of the substances burned.

To see whether the higher oxides of nitrogen are formed in the flameless combustion of solids, he heated, both in pure air and in oxygen, in a suitable tube, magnesium, zinc, and iron reduced by hydrogen; both nitrous and nitric acid are formed in all cases. Ilosvay wishes to experiment further before expressing an opinion whether in these cases the formation depends on the temperature or not.

One might suppose that on uniting in a eudiometer dry hydrogen and dry oxygen in presence of an excess of oxygen, hydrogen peroxide could be formed as a secondary product, and that ozone might be formed when carbon monoxide unites with oxygen in presence of an excess of oxygen. The author purified and dried these gases, introduced them into eudiometers over dry mercury, and exploded them. No matter in what proportions the gases were mixed, no hydrogen peroxide nor ozone was formed, but in all cases *nitrous* and *nitric* acids. He says that of course his gases must have contained traces of air, the nitrogen of which was oxidised. The difficulty of getting gases absolutely free from air is known to chemists, and Ilosvay thinks it extremely difficult, if not impossible, to remove the last traces of air, as in these experiments he worked with every known refinement and precaution. The author asks whether the oxides of nitrogen are not a more important constituent of the air and of vegetable growth than now supposed, whether reactions attributed to ozone and hydrogen peroxide are not caused entirely or in part by nitrous acid.

The fifth paper answers the question, Does the air contain ozone or hydrogen peroxide? Ozone is supposed to be formed by active and slow combustion, by electric discharges in the air, and in the evaporation of water. It is supposed that in slow combustion hydrogen peroxide is also formed. The author has not succeeded in finding ozone among the products of active combustion, nor on the evaporation of water. In passing an electric spark through air ozone is not formed, but he finds nitrous acid, thus confirming the observations of Cavendish and those of Böttger.¹

¹ Jahresbericht, 1858, 102.

Slow combustion, as in the decay of vegetable matter, cannot form ozone, because if it did we should find most ozone near the soil. Hartley and Scontellen¹ have shown that it is not found there. By the action of a Holtz electric machine ozone and the higher oxides of nitrogen are both formed, and the author thinks it probable that if ozone is formed in the air it must be by silent electric discharges.

Ilosvay bases his tests on the results of two previous experiments:

1. Hydrogen peroxide oxidises alkali nitrite to nitrate, and if present in excess can be recognised by titanous acid.
2. Ozonised air passed through a 20 per cent. solution of sulphuric acid and a 4 per cent. solution of sodium hydroxide reacts quickly with the amido-azo compound, with thallium suboxide and with potassium iodide.

The apparatus used consisted of:

1. A Winkler absorption tube with 20 per cent. NaOH;
2. A Pettenkofer tube 550 cm. long containing 20 per cent. H_2SO_4 ;
3. A Pettenkofer tube a meter long containing 4 per cent. sodium hydroxide;
4. A small Peligot tube with 4 per cent. sodium hydroxide;
5. A Winkler absorption tube containing a dilute solution of amido-azo color;
6. A small empty Peligot tube;
7. A Winkler tube containing potassium iodide;
8. A straight tube containing protoxide of thallium paper, and Wurster's tetra-methyl-phenylene-diamine paper;
9. A small Peligot tube containing strong sodium hydroxide;
10. A straight tube with Lender's ozonometer;
11. A washing bottle with soda;
12. A gas meter;
13. A water pump.

All the apparatus and connections were of glass and constructed with such care that when the whole system was connected it held a column of mercury 534 mm. high for several hours. The parts containing reagents were protected from the light by black cloths; the air was pumped from outside the window of the laboratory. The first experiment lasted fifteen days and nights. 774,244 liters of air were drawn through the apparatus. The second experiment lasted five days and nights, and 500 liters of air were drawn through the apparatus. The result of these trials was that no ozone was detected. In the first Winkler tube nitrous and nitric acids and traces of ammonia were found; in the sulphuric acid tube a little ammonia; in the Pettenkofer tube, containing 4 per cent. sodium hydroxide, very little nitrous and nitric acids and still less ammonia; in the small Peligot tube filled with sodium

¹ Fehling, *Handwörterbuch* 4, 1087.

hydroxide minute traces of these three compounds. The first three tubes were examined for hydrogen peroxide, but none was found.

These experiments were made in May and June; the weather was fine with frequent thunder-storms, and was such as is supposed to be favorable to the formation of ozone and hydrogen peroxide.

Single tests made on mountains, in the country and in the city, under varied conditions of weather, confirm these results. The author says that he finds more nitrous acid in the air in spring than in the autumn; more in the day-time than at night; and that the amount increases with the height of the layers of air. He wishes this paper to be considered preliminary.

In his sixth paper he confirms Schönbein's statement that saliva contains nitrous acid, and Struve's statement that the air exhaled from the lungs contains ammonium nitrite, and he also shows that the air exhaled by animals contains more nitrous acid than ordinary air.

In the November number of the *Bulletin*, Ilosvay has a short article on the presence of nitrous acid in the air. Grass and the leaves of trees cut in the morning while covered with dew were washed with pure water; the water then gave the reaction for nitrous acid. Grass cut at noon and in the evening yielded no nitrous acid, unless the day had been cloudy without rain. Nitric acid and ammonia were always found, no matter when the grass was cut. These results were confirmed by numerous experiments, and Ilosvay concludes that either nitrites or nitrates are always present on the surface of plants; but that in dry clear weather nitrites are oxidised to nitrates either by oxygen escaping from the pores of the leaves or by oxygen of the air aided by the action of the sun's rays.

Specimens of sand, sandy soil and loam containing much humus were washed until free from oxides of nitrogen, carefully dried and exposed to the air. At the end of twelve hours all the specimens gave the reactions for nitrous and nitric acids and ammonia. In a parallel series of experiments, air freed of oxides of nitrogen was conducted over specimens of the dried soils, and no nitrites, nitrates, nor ammonia were formed. This shows that the soil takes up nitrous and nitric acids and ammonia directly from the air, and suggests that the nitrites and nitrates contained in the air, whatever their source, help to furnish the nitrogen necessary for plant life.

In the *Bulletin* of Dec. 5th, 1889, Ilosvay gives the details of several additional interesting experiments. Böttger¹ has affirmed that the oxygen made by the action of concentrated sulphuric acid on potassium permanganate contains ozone. Leeds² on the other hand maintains that ozone is not formed in this reaction, and that the reactions ascribed by Böttger to ozone were due to chlorine

¹ Jahresbericht, 1862, 44.

² Chemical News 39, 18.

contained in the permanganate. Ilosvay treated dry permanganate with concentrated sulphuric acid. Both reagents were shown to contain no chlorine; the oxygen generated was passed through three absorption tubes containing respectively water, a solution of the amido azo-dye, and a dilute solution of potassium iodide and starch paste. The violet-colored gas passed through the water, coloring it rose; it turned the dye yellow, and set iodine free. No chlorine being present, these reactions suggested ozone; but the author found that a dilute aqueous solution of pure potassium permanganate, as well as free chlorine or ozone, turns the azo-dye yellow, and sets free the iodine of a perfectly neutral or slightly acidulated solution of potassium iodide. This led him to suppose that the oxidising action in the above experiment might be due to permanganic anhydride, Mn_2O_7 . By repeating the experiment, passing the oxygen first through two wash-bottles so as completely to absorb all permanganic anhydride, he found that neither the azo-dye, the potassium iodide, nor thallium oxide paper is affected by the oxygen; but if this precaution is not taken, one can obtain every reaction by which ozone is characterised; *i. e.*, in addition to those mentioned, the bleaching of indigo solution, the production of silver peroxide on metallic silver, the oxidation of lead hydroxide to lead peroxide, and that of lead sulphide to lead sulphate. The author therefore concludes that the reactions attributed to ozone in the action of sulphuric acid on permanganate may be due to chlorine if the permanganate contains chlorine, but that, otherwise, they are due to permanganic anhydride, and that no ozone is formed.

The author then examined the oxygen produced by the action of concentrated sulphuric acid on potassium dichromate, and found the characteristic ozone reactions; but shows that they are caused by chlorine contained in the dichromate. After so modifying his apparatus as completely to absorb the chlorine, the oxygen passed for an hour and a half over the reagents without acting on them.

Led by observations which showed that at high temperatures nitrogen has much affinity for hydrogen, oxygen, and carbon, forming ammonia, nitrous and nitric acids, and cyanogen, the author conducted pure air over heated platinum in the form of foil, of sponge, and of platinum black. In each of these forms platinum has the property of causing the union of nitrogen with oxygen at comparatively low temperatures, forming nitrous acid, as proved by the usual reagents. No ozone is formed. With platinum foil the action takes place between 280° and 350° ; but, after heating an hour and a half, the platinum loses the property of causing union of nitrogen and oxygen. With platinum black the action commenced at 180° , was most marked at 250° , and diminished rapidly above 300° . With platinum sponge action began at 250° , was strongest at 300° , and diminished above 350° . After use, both the black and sponge lose the power of causing action. After some time, however, all kinds of platinum regain the power.

To test the ease with which nitrogen unites with oxygen, the author reduced ferric oxide to iron, by heating it in a tube in a current of hydrogen at a temperature not above 350° . After it had cooled in a current of hydrogen he heated it in the same tube in a current of dry pure air. At 190° the iron commenced to absorb some of the air passing over it. This absorption continued up to 250° . The air passing over the iron was conducted through a solution of pure sodium hydroxide. After heating for an hour, the sodium hydroxide was shown to contain minute traces of nitrous acid, but the iron oxide formed in the tube when treated with water gave a strong reaction for nitrous acid. That the iron oxide contains either nitrates or nitrites of iron is shown by again reducing it in a current of hydrogen, when aqueous vapor and ammonia escape with the hydrogen.

The author notes that iron reduced by hydrogen does not become incandescent in a current of dry air, even at a temperature of 400° ; but in contact with moist air it becomes incandescent at 100° . Consequently the quick oxidation of iron depends not only on the fine division of the metal and the temperature at which it has been reduced, but also on the moisture in the air.

E. RENOUF.

ALLOTROPIC FORMS OF SILVER.

The May number of this Journal contains an abstract of M. Carey Lea's first article on the Allotropic Forms of Silver. He has since published three supplementary articles,¹ giving the results of his further work on the subject. Since writing his first paper he has spent much time in determining definitely whether the solubility of his first allotropic form *A* is due to a combination of the silver with citric acid.

"Many attempts were made to get a decisive indication, and two series of analyses, one a long one, to determine the ratio between the silver and the citric acid present, without obtaining a wholly satisfactory result, inasmuch as even these determinations of mere ratio involved a certain degree of previous purification which might have caused a separation.

"This question has since been settled in an extremely simple way, and the fact established that the soluble blue substance contains not a trace of combined citric acid.

"The precipitated lilac-blue substance (obtained by reducing silver citrate by ferrous citrate) was thrown on a filter and cleared of mother-water as far as possible with a filter pump. Pure water was then poured on in successive portions until more than half the substance was dissolved. The residue, evidently quite unchanged, was of course tolerably free from mother-water. It was found that by evaporating it to dryness over a water-bath most of the

¹ *Am. Jour. of Sci.* **38**, 47, 129, 237.

silver separated out as bright white normal silver; by adding water and evaporating a second time, the separation was complete, and water added dissolved no silver. *The solution thus obtained was neutral.* It must have been acid had any citric acid been combined originally with the silver. This experiment, repeated with every precaution, seems conclusive. The ferrous solution used for reducing the silver citrate had been brought to exact neutrality with sodium hydroxide. After the reduction had been effected, the mother-water over the lilac-blue precipitate was neutral or faintly acid.

"A corroborating indication is the following. The portions of the lilac-blue substance which were dissolved on the filter (see above) were received into a dilute solution of magnesium sulphate, which throws down insoluble allotropic silver of the form I have called *B* (see previous paper). This form has already been shown to be nearly pure silver. The magnesia solution, neutral before use, was also neutral after it had effected the precipitation, indicating that no citric acid had been set free in the precipitation of the silver.

"It seems therefore clear that the lilac-blue substance contains no combined citric acid. Had the solubility of the silver been due to combination with either acid or alkali, the liquid from which it was separated by digestion at or below 100° C. must have been acid or alkaline; it could not have been neutral.

"We have therefore this alternative. In the lilac-blue substance we have either pure silver in a soluble form, or else a compound of silver with a perfectly neutral substance generated from citric acid in the reaction which leads to the formation of the lilac-blue substance."

The later papers add several interesting points in reference to the properties of allotropic silver.

"The three forms of allotropic silver which were described in the June number of this journal—the blue soluble and the blue and the yellow insoluble—are not to be understood as the only forms which exist, but as the best marked only. The substance is protean and exhibits other modifications not yet studied. No other metal than silver appears to be capable of assuming such a remarkable variety of appearances. Every color is represented. I have obtained metallic silver blue, green (many shades of both), red, yellow, and purple. In enumerating these colors I do not refer to interference colors produced superficially by reagents, also wonderfully brilliant, but to body colors. As a single instance of coloration, the following may be mentioned: I recently obtained a solution of allotropic silver of an intense yellow brown. A little solution of disodic phosphate changed this to bright scarlet (like Biberich scarlet), presently decolorising with formation of a purple precipitate. Washed on a filter this changed to bluish green. The colors I have met with in this investigation can only

be compared with the coal-tar products, of which one is constantly reminded by their vividness and intense colorific power."

It is found that the superficial color reactions, mentioned in the first paper, can be obtained by other reagents than the halogen compounds there mentioned.

"Paper brushed over with either the gold, the copper-colored, or the bluish green substance exposed to the vapor of *ammonium sulphide*, or immersed in a dilute solution of it, assumes beautiful hues, though less brilliant than those obtained in some other ways.

"Potassium permanganate in dilute solution produces blue, red, and green colors.

"Potassium ferricyanide in moderately strong solution gradually attacks allotropic silver, with production of splendid blue, purple, and green coloration.

"Phosphorous acid produces gradually a rather dull coloration.

"The color reaction is produced finely by substances which readily part with a halogen, such as ferric and cupric chlorides, sodium hypochlorite, hydrochloric acid to which potassium bichromate has been added, and by corresponding bromine and iodine compounds. . . .

"The perchlorides of platinum, gold, and tin do not give the color reaction, though by analogy one would expect that they should, since they can lose chlorine with formation of a lower chloride."

When the silver is in a pure condition the alkaline haloids do not give the color reaction, as was at first supposed.

"The two insoluble forms of allotropic silver, described as *B* and *C*; *B*, bluish green, *C*, rich golden color—show the following curious reaction. A film of *B*, spread on glass and heated in a water stove to 100° C. for a few minutes, becomes superficially bright yellow. A similar film of the gold-colored substance *C* treated in the same way acquires a blue bloom. In both cases it is the surface only that changes."

All the forms of allotropic silver are sensitive to light. *A* when exposed to the sunlight soon becomes brown. The bright blue-green variety of *B* is changed into the pure gold-colored variety of *C*. Other forms of *B* turn brown on exposure to light.

The red-yellow variety of *C* changes to bright gold color. "Continued exposure seems to produce little further change so long as the substance is dry. But if the paper on which the silver is extended is kept moist by a wet pad, with three or four days of good sunshine, the change goes on until the silver becomes perfectly white, is apparently changed to normal silver: water, alone, tends to darken this form of allotropic silver, accordingly the portion of the paper that was protected for comparison darkened, showing that the whitening effect was due wholly to light. . . .

"The white silver thus obtained has all the character of ordinary silver and does not show the color reaction with ferric and cupric chloride, potassium ferricyanide, etc. Just in proportion to the exposure to light, the ability to give the color reaction diminishes, so that after a day's exposure, when the exposed part has become bright yellow, the color reagents scarcely affect this yellow, whilst the protected part becomes intense blue, purple or green. In this way it is easy to observe the gradual effect of light as it changes the allotropic silver, finally converting it into what resembles in every way, and is undoubtedly, ordinary silver."

The specific gravity of the forms *B* and *C* was found by careful determinations to be less than that of normal silver. $B = 9.58$, $C = 8.51$, normal silver $= 10.5$, or 10.62 when in the condition of a finely divided precipitate.

In reference to physical condition the author says: "The brittleness of the substances *B* and *C*, the facility with which they can be reduced to the finest powder, makes a striking point of difference between allotropic and normal silver. It is probable that normal silver, precipitated in fine powder and set aside moist to dry gradually, may cohere into brittle lumps, but these would be mere aggregations of discontinuous material. With allotropic silver the case is very different, the particles dry in optical contact with each other, the surfaces are brilliant and the material evidently continuous. That this should be brittle indicates a totally different state of molecular constitution from that of normal silver. . . .

"When gold-colored allotropic silver is gently heated in a test-tube it undergoes a remarkable change in cohesion. Before heating it is brittle and easily reduced to fine powder. After heating it has greatly increased in toughness and cannot be pulverised at all."

Both the insoluble forms *B* and *C* resemble normal silver in disengaging oxygen from hydrogen dioxide.

All the forms are much more sensitive to light than ordinary silver.

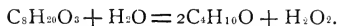
W. V. METCALF.

NOTES.

Absorption of Nitrogen during Slow Oxidation.

In the August (1889) number of the *Annales de Chimie et de Physique*, M. Berthelot gives the results of some experiments upon the absorption of nitrogen during processes of slow oxidation, as in the case of the soil and of plants. It has been found

that certain substances, as, for example, ether, turpentine, certain aldehydes, oleic acid, etc., possess the power of absorbing free oxygen, and when brought into contact with some substance capable of easy oxidation, again yielding it up in such way as to bring about this oxidation. Thus potassium iodide is oxidised by treating it with ether which has stood a long time in contact with air. If pure water be shaken with such ether, it will act, after separation from the ether, like a solution of hydrogen peroxide when brought into the presence of chromates. According to M. Berthelot, by exposure to the air ether becomes converted into an oxidation product, $C_8H_{20}O_3$, and this decomposes in the presence of water:



If ether which has stood in contact with the air a long time be treated with lime-water absolutely free from nitrates, the aqueous solution on evaporation yields a residue which with ferrous sulphate and strong sulphuric acid reveals the presence of nitric acid. If carefully purified ether be allowed to stand in contact with pure water or with pure lime-water for a considerable length of time, a trace of nitric acid is formed. Passage of air, bubble by bubble, through pure ether produces the same result. Ether can thus convert a minute portion of the nitrogen of the air into nitric acid. In the case of turpentine the detection of the nitric acid is difficult, since strong sulphuric acid acts upon the aqueous solution of the products of the oxidation of the turpentine, forming an intense yellow color which masks that due to nitric acid. M. Berthelot comes to the conclusion that, in the case of turpentine, mesitylene, benzoic aldehyde, and oleic acid, if the formation of nitric acid does take place, the quantity is no greater than in the case of ether. Experiments undertaken to discover whether ammonia is formed in the oxidation of iron by means of pure water gave no positive results; the fact that the iron used often contains a trace of combined nitrogen prevents the experimenter from coming to any definite conclusion with regard to the matter.

W. W. RANDALL.

AMERICAN CHEMICAL JOURNAL.

REVISION OF THE ATOMIC WEIGHT OF GOLD.¹

BY J. W. MALLET, F. R. S.,

Professor of Chemistry in the University of Virginia.

Until lately gold ranked among the elementary substances of which the general properties had been well ascertained, but in regard to the atomic weights of which our knowledge was least satisfactory. That this constant should be determined as accurately as possible for gold was desirable in view of its bearing on the precise place assigned the metal in the "periodic" classification of the elements based on the ideas of Newlands, Odling, Mendelejeff, and L. Meyer. Furthermore, an exact knowledge of the atomic weight of gold might be conveniently applied in the determination of the atomic weights of some of the other elements. A practical laboratory reason for desiring to possess a trustworthy value for this constant was also presented by the facility with which gold compounds of many organic substances may be prepared, and the ease with which their composition may be ascertained by simple ignition in the air and weighing of the residual gold, the results leading to a knowledge of molecular composition when the atomic value of the weight of the metal obtained is assumed to be known.

For the last three years and a half I have been occupied, during a large part of such time as has been available for original work,

¹ From the Philosophical Transactions of the Royal Society of London, 180 (1889), A, pp. 395-441.

in devising and carrying out experiments aiming at the redetermination of the constant in question. The difficulties met with have been greater than were at first looked for, and have led to much time and labor being consumed in attempts to overcome them. About two years ago, when this work was already well under way but still in progress, there appeared the results of experiments aiming at the same end, by Krüss in Germany and by Thorpe and Laurie in England—experiments made with the care and accuracy of modern methods, and apparently deserving of much confidence. My own work, however, was continued, as we cannot have too many careful independent determinations of atomic weights by different workers, and as I had used to a considerable extent other processes than those on which the newly published determinations were based, while the chemists named had employed, in the main, one and the same method. A preliminary notice of my work was read in the Chemical Section of the British Association at the Manchester meeting of 1887. The details of my experiments and the results which I have reached are now laid before the Royal Society.

Earlier Determinations of the Atomic Weight of Gold.

In the work of L. Mulder, "Historisch-kritisch Overzicht van de Bepalingen der *Æquivalent-Gewigten* van 24 Metalen," Utrecht, 1853, and in the recent papers of Krüss and of Thorpe and Laurie, there are abstracts of reports upon a number of experiments by chemists of the earlier part of this century, bearing on the value to be assigned to the atomic weight of gold, such as those of Proust,¹ Richter,² Dalton,³ Thomson,⁴ Oberkampf,⁵ Pelletier,⁶ Figuier,⁷ and Javal;⁸ but of these none deserve any attentive consideration at the present day, the methods used having in some cases been such that accurate results could not be expected from them, and the actual figures obtained in other cases differing so widely from each other that no importance can be attached to them.

Before the year 1887 but two chemists—Berzelius and Levöl—had published the results of experiments furnishing fairly admissible data for calculating the atomic weight in question.

¹ *Journal de Physique* **62** (1806), 131; N. Gehlen, *Journal* **1** (1806), 477.

² Schweigger, *Journal* **7**, (1813), 43.

⁵ *Annales de Chimie* **80** (1811), 140.

³ *New System*, Part 2 (1810), 253.

⁶ *Ib.* **15** (1820), 5, 113.

⁴ *First Principles* **1** (1825), 440.

⁷ *Ib.* **19** (1821), 177.

⁸ *Ib.* **17** (1821), 337; Schweigger, *Journal* **33** (1821), 238.

A. *Experiments of Berzelius*, 1813.¹—The method adopted was the precipitation of a solution of auric chloride by metallic mercury, determining the quantities of mercury dissolved and gold thrown down. In the original paper but a single experiment is reported, but later the author appears to have made a second,² so that for the two Meyer and Seubert, in their recalculation of the atomic weights of the elements,³ give as the sums of the amounts of mercury and gold found to be equivalent to each other 24.240 grams of the former and 15.912 grams of the latter. Taking these quantities to represent the ratio between the weights of three atoms of mercury and two atoms of gold, we have for the weight of the single atom of the latter ($H = 1$):

If we assume $Hg = 199.8$ (L. Meyer and Seubert), ³	196.73
“ “ “ = 199.712 (F. W. Clarke), ⁴	196.65

This method recommends itself as advantageous on several grounds, and the experiment deserves repetition as soon as the atomic weight of mercury becomes known with greater certainty than at present. But until this condition is fulfilled, the result for gold cannot be depended upon as of the first rank in exactness. In any renewed attempt to apply this method several questions would have to be examined as to the precise nature of the solution used, and of the reaction itself.

[Berzelius⁵ also precipitated gold by means of a known quantity of phosphorus from a solution of the chloride used in excess, and his results, as calculated by F. W. Clarke,⁶ lead to the atomic weight 195.303 for gold; but this process appears ill adapted to give very exact results, even in such hands as those of the great Swedish chemist, and the value obtained is certainly too low in the light of more modern researches.]

B. *Experiments of Berzelius*, 1844.⁷—In these experiments potassium auri-chloride, which, it was found, could not be completely dried without loss of chlorine, was ignited in hydrogen, and the residue was treated with water to dissolve potassium

¹ Stockholm, Kgl. Vetensk. Akad. Handl., 1813, 185.

² Berzelius, Lehrbuch 3, p. 1212, str. 70.

³ Lothar Meyer u. Karl Seubert, Die Atomgewichte d. Elemente aus d. Originalzahlen berechnet, Leipzig, 1883, 191.

⁴ “The Constants of Nature,” Smithsonian Miscellaneous Collections, Washington, D. C.

⁵ Berzelius, Lehrbuch, 5. Aufl. 3, 1188.

⁶ “The Constants of Nature,” Smithsonian Miscellaneous Collections, Washington, D. C.

⁷ Berzelius, Lehrbuch, 5. Aufl. 3, 1212.

chloride, the quantity of which was determined, as well as that of the metallic gold left undissolved. Five experiments were made, and the aggregate amounts obtained of potassium chloride and gold were 3.7800 grams and 9.9685 grams respectively. These figures, if we assume $K = 39.03$ and $Cl = 35.37$, give for the atomic weight of gold 196.20, the lowest result from one of the individual experiments being 196.11, and the highest 196.27.

Among possible sources of error in this process we may note as deserving consideration the conceivable retention by the potassium auri-chloride of hydrogen auri-chloride, and the difficulty of directly determining with accuracy the potassium chloride extracted by water. The former would lead to a higher result for gold than should be obtained; the latter might either give too low a result in consequence of imperfect drying, or too high if there were partial loss by volatilisation, either during the ignition in hydrogen or in subsequently recovering the potassium chloride from solution. The quantities of material used were smaller than is probably desirable.

C. *Experiments of Levol*, 1850.¹—A weighed quantity of gold was dissolved as auric chloride, the metal reduced from the solution by means of sulphur dioxide, and the sulphuric acid formed was determined as barium sulphate. In two experiments, reported as giving exactly the same result, 1 gram of gold gave 1.782 gram of barium sulphate. Hence, if Ba be taken $= 136.86$, S $= 31.98$, and O $= 15.96$, we have for the atomic weight of gold the number 195.86.

Of the sources of error to which this method is liable probably the most important are atmospheric oxidation of sulphurous to sulphuric acid and imperfect washing out of soluble compounds of barium from the barium sulphate. Both would tend to give too low a result for gold.

For all these earlier experiments details are wanting as to the exact mode of purification of the gold and other materials used, and in the weighings there appears to have been no correction introduced for atmospheric buoyancy; the results doubtless represent apparent, not absolute, weights.

[There is also to be quoted the statement of Julius Thomsen,² that he found in hydrogen brom-aurate ($AuBr_3 \cdot HBr \cdot 5H_2O$) 32.11 per cent. of gold and 52.00 per cent. of bromine, from which he

¹ *Annales de Chimie* [3] **30**, 355.

² *J. prakt. Chem.* **13** (1876), 345.

concluded that $\text{Au} \equiv$ probably about 197. Taking $\text{Br} \equiv 79.76$, and calculating from the ratio of $\text{Br}_4:\text{Au}$, the number is 197.01.]

Recent Careful Determinations of the Atomic Weight of Gold.

A. *Experiments of Gerhard Krüss, 1886.*¹—The author has described in detail the means resorted to for the preparation of pure metallic gold, and especially for its separation from silver and the metals of the platinum group, with an account of the spectroscopic examination of the gold employed. He has then given a full account of: *a.* His determinations of the gold and chlorine (the former reduced by a stream of sulphur dioxide; the latter precipitated and weighed as silver chloride) in a neutral solution of auric chloride, prepared by the action of water on the so-called auro-auric chloride (Au_2Cl_4),² itself prepared by the direct action of chlorine on metallic gold; *b.* Like determinations of gold and chlorine in sublimed auric chloride, made by direct action of the elements on each other with careful regulation of the temperature; *c.* Determinations of the gold in a weighed quantity of potassium auri-bromide (KAuBr_4), the metal in some experiments reduced from a solution of the salt by sulphurous acid, in others reduced from the dry salt by heating in a stream of hydrogen; *d.* Determinations of the gold and bromine (the former thrown down by sulphurous acid; the latter precipitated as silver bromide) in the same salt, potassium auri-bromide; *e.* Determinations of the loss of weight (representing 3 atoms of bromine for 1 of gold) undergone by heating potassium auri-bromide gradually to 320°C ., towards the end in a stream of hydrogen; *f.* Determinations of the quantity of potassium bromide recovered from the residue left in the experiments of *e* by treatment of this residue with water, separation of the metallic gold, careful evaporation of the liquid, and final cautious heating of the potassium bromide over a free flame. In the experiments of series *a* account was taken of the somewhat different processes of purification of the gold used, but, no corresponding differences being observable in the results obtained, no further record was made in the remaining series of the history of the gold used in these.

¹ Ann. Chem. (Liebig) **238**, 30; and separate publication, G. Krüss, Untersuchungen über das Atomgewicht des Goldes, München, 1886.

² Krüss has in a later paper (Ber. d. chem. Ges. **20**, 2634) denied the existence of auro-auric chloride as a definite compound, but admits that the substance so described by Julius Thomsen yields on treatment with warm water a solution of pure neutral auric chloride, with separation of metallic gold.

After correction of the weighings for atmospheric buoyancy in such cases as seemed to the author to involve a correction worth noticing, the following results were calculated from the figures obtained, these figures agreeing in general closely with each other in each series :

Series <i>a</i> .	Mean of 8 experiments.	At. weight of gold = 196.622
" <i>b</i> .	" 4	" " " = 196.143
" <i>c</i> .	" 9	" " " = 196.741
" <i>d</i> .	" 5	" " " = 196.743
" <i>e</i> .	" 4	" " " = 196.619
" <i>f</i> .	" 4	" " " = 196.620

Leaving out the results of series *b* on the ground of the very small quantity of sublimed auric chloride available, and the considerable discrepancy of one of the results (that in which most material was used) from the rest, the author calculates from the remaining 30 experiments the general mean 196.669; but, taking into account the greater or less closeness of agreement of the figures obtained by the several methods, he comes to the conclusion that 196.64 may better be assumed as the true atomic weight of gold. In these calculations Ag was assumed = 107.660, Cl = 35.368, Br = 79.750, and K = 39.040.

As regards possible sources of constant error in Krüss's experiments, it may be observed that—

1. In series *b* very small quantities of sublimed auric chloride were used—the whole amount available for all four experiments being only about seven-tenths of a gram—and it is probable that a little free chlorine may have been physically retained by the chloride in spite of the long-continued passage over it of dry air. The experiment in which the largest quantity of material was used gave the atomic weight = but 194.79. On these grounds the author himself excludes the series from consideration in calculating his general mean.

2. In series *c*, *d*, and *e* the evidence is pretty strong, but perhaps not conclusive, to show that potassium auri-bromide can be rendered absolutely dry by exposure to air in a vessel containing phosphorus pentoxide, either at ordinary or higher temperatures, without, at the same time, undergoing any loss of bromine. The attainment of constant weight by the salt does not positively prove the entire removal of water. If moisture were retained the atomic weight of gold found would be brought out lower than it should be.

3. Krüss himself observed that in all cases in which he dissolved potassium auri-bromide in water a small residue of metallic gold was left, and, determining in a single experiment the amount of this (about .05 per cent.), he used it as a correction for all his results. As pointed out by Thorpe and Laurie,¹ this partial decomposition of the salt was probably due to the action of dust from the air. If the results obtained from the solution were used, without any correction, to establish the atomic weight of gold, the tendency would of course be to a value lower than the truth. Although the correction introduced is small, it can hardly be supposed that it should be taken as constant in amount in all the experiments.

4. In series *e* it may be questioned whether traces of potassium bromide may not have been volatilised at the highest temperature used, or the residual potassium bromide may not have, to a small extent, exchanged bromine for oxygen while heated in air (before the use of the stream of hydrogen), the latter change being one to be guarded against whenever haloid salts are strongly heated in the presence of free oxygen. The tendency in both cases would be to a lower atomic weight for gold.

5. In series *f* there was risk of slight loss of potassium bromide during filtration and evaporation of its solution, and during exposure of the salt to the heat of a free flame, when there might possibly have been again slight replacement of bromine by oxygen, thus causing the atomic weight sought to come out too high, or else, on the other hand, risk of imperfect drying, which would give too low a value for the atomic weight in question.

On the whole it seems probable that the tendency of most of the constant errors to be suspected in connection with Krüss's experiments—experiments carried out with remarkable patience, skill, and apparent freedom from merely "fortuitous" errors—was in the direction of an atomic weight for gold somewhat below, rather than above, the true value.

B. *Experiments of Thorpe and Laurie, 1887.*²—In these experiments potassium auri-bromide was used, and determinations were made: *a.* Of the weight of the residue left on heating the salt over a Bunsen flame till bromine ceased to be given off (this residue consisting of metallic gold and potassium bromide), and

¹ Chem. Soc. Journ., Dec., 1887, p. 866.

² Ibid., June, 1887, p. 565, and Dec., 1887, p. 866.

the weight of the gold left by such residue after all potassium bromide had been washed out of it by water; *b*. Of the weight of silver necessary to be added as nitrate to the solution of potassium bromide obtained in *a* in order to just precipitate the bromine present; *c*. Of the weight of the silver bromide so precipitated. All suitable experimental precautions seem to have been taken, and the weighings were corrected for atmospheric buoyancy. The individual results in each series agreed with each other even more closely than in Krüss's research.

The results obtained were as follows, using in calculation the numbers $\text{Ag} = 107.66$, $\text{Br} = 79.75$, and $\text{K} = 39.03$:

Series <i>a</i> .	Mean of 8 experiments.	At. weight of gold	= 196.876
" <i>b</i> .	" 9	" " "	= 196.837
" <i>c</i> .	" 8	" " "	= 196.842

The general mean of these values, giving equal weight to the different series, is 196.852.

As regards possible sources of constant error specially belonging to these experiments, it is to be noticed—

1. There is an advantage, as observed by the authors themselves, over the greater part of the experiments of Krüss, in the nature of the relations employed not requiring that the potassium auribromide should be perfectly dry, the exact quantity of the original salt not needing, in fact, to be known.

2. In series *a* it is conceivable that there might have been slight volatilisation of potassium bromide, or interchange in it to a small extent of bromine for oxygen, during the heating of the original salt, or retention of traces of potassium bromide by the metallic gold when washed—the latter but little probable. Any of these defects, if existing, would cause the method to give a higher value for Au than the true one.

3. In series *b* the probability seems to be in favor of not quite the whole of the original potassium bromide being actually used, and minute loss of silver solution having perhaps occurred, so that rather more of this solution was counted as used than the true quantity. If so, the former defect would tend to raise, the latter to lower, the atomic weight of gold.

4. In series *c*, in view of the evidence adduced to prove complete drying of the silver bromide, it is more likely that its weight as obtained was below, rather than above, the truth. Hence we

should suspect, if any constant error exist, that it would rather tend towards an unduly high value for Au.

On the whole, there seems to be less reason to fear sources of constant error of any considerable amount in connection with the experiments of Thorpe and Laurie than with those of Krüss, and the drift is in the opposite direction, tending rather to give too high than too low a value for the atomic weight to be determined.

It should be mentioned that Krüss¹ has claimed that in the potassium auri-bromide used by Thorpe and Laurie there was probably as much free gold as he considered to exist in the salt used by himself, and on this assumption has calculated that the three series of experiments by the English chemists should, if corrected on this account, lead to the numbers 196.616, 196.559, and 196.575 respectively for Au. From this conclusion the latter chemists altogether dissent,² and express their confidence that in none of the preparations used by them was there free gold sufficient to account for the difference between their own results and those of Krüss.

General Results of Former Determinations most deserving Confidence.

These recent researches, unquestionably by far the most valuable up to the present time, give us, when taken separately and together, the following values for the atomic weight of gold:

- | | | | |
|----|---|------------------------------|---------|
| 1. | General mean of 5 series by Krüss, as calculated by | | |
| | | himself | 196.640 |
| 2. | “ “ 3 series by Thorpe and Laurie, as | | |
| | | calculated by themselves . . | 196.852 |
| 3. | “ “ 1 and 2, giving equal value to each, | | 196.746 |

Difficulties to be overcome in Determining the Atomic Weight of Gold.

Besides the special difficulties connected with each method which may be adopted, the determination of any high atomic weight with a degree of accuracy which enables the result to be accepted to a given decimal place is clearly a much less easy matter than would be the attainment of an apparently equal degree of precision for an atomic weight represented by a small number. In obtaining the atomic weight of lithium, the first with which, many years ago,

¹ Ber. d. chem. Ges. 20, 2365.

² Chem. Soc. Journ., Dec. 1887, p. 868.

I had any personal experience, a difference of unity in the first decimal place corresponded to about $\frac{1}{70}$ th of the whole value considered to be correct. In getting the atomic weight of aluminum, worked on later, a like difference represented approximately $\frac{1}{270}$ th of the whole value. But, in the case now considered, of the atomic weight of gold, unity in the first decimal place means but about $\frac{1}{1970}$ th of the whole value. So that, looking at the matter in this light, it may be said that a degree of precision is demanded more than seven times as great as in the case of aluminum, and twenty-eight times as great as in the case of lithium.

There is also to be noticed, as the most obvious *general* difficulty to which all methods for determining the atomic weight of gold are more or less exposed, the instability of compounds of this metal; not merely the ease with which complete decomposition occurs, with separation of free gold, but the much more insidious and less easily detected trouble arising from the comparative ease with which aurous pass into auric compounds, and the reverse.

New Experiments by the Author.

The general difficulties just alluded to, and the special points to be investigated in regard to each method of determination tried, have demanded much time and work, and I cannot feel even now that all has been done that is desirable and possible; but the experiments projected have been so far completed as to seem to justify publication, and I am not likely soon to be able materially to extend them.

General Principles kept in View.

The improvements made of late years in manipulative methods and apparatus have tended to reduce very much the magnitude of what are commonly called "fortuitous" errors in our quantitative determinations of matter, and to increase greatly the accuracy of such determinations. Probably no modern work has had more influence in this direction than the classic researches of Stas on certain atomic weights—the precautions taken by him, and his remarkable manipulative skill, causing his results to bear almost the same relation to those of his immediate predecessors as did those of Berzelius to the work of the chemists of his earlier day. No one nowadays would undertake the determination of an atomic weight of one of the better known elements without taking such

elaborate precautions as practically ensure pretty close concordance of results, when obtained by the same method, applied in the same hands. In the present state of the question of atomic weights and improvements in their determination, advances in mere delicacy of manipulation and success in merely securing close agreement of results by the same method are not alone sufficient. It cannot be too much insisted upon that we need, besides, well-directed and laborious investigation of possible sources of *constant errors*, and the adoption of means to guard against them. Careful preliminary study is required, in a general way, of the precise nature of each reaction employed, and how it may be influenced by the conditions of the experiment. We learn more and more of late that many of the reactions—perhaps it should rather be said of all the reactions—which have been generally supposed to be of the simplest nature are in reality complex.

The following are among the general principles which seem to be most important, as tending to greater accuracy and trustworthiness in atomic weight determinations; they have been in part stated in the author's earlier paper on the atomic weight of aluminum:

1. In purifying the materials used, both the element of which the atomic weight is to be investigated (or any special compound containing it) and all substances used to react thereupon, resort should in all cases be had to "fractional" methods, assuming materials to be pure only when earlier and later fractions give no signs of any constant difference in the results which they yield.

2. Different and independent processes should be applied to the determination of the same atomic weight, and the results used to check each other. It is desirable that as many such different processes be applied as can be devised, provided each be reasonably free from apparent sources of error, even though it be usually impossible to properly assume that all are equally advantageous in this respect, and therefore of equal value. In the comparison of results obtained it should be noticed whether a given method tends on the whole to yield results probably higher or lower than the truth, though it may be gravely doubted whether the practice is commendable of attempting any numerical estimate of relative value, by so-called "weighting" of the results in calculation.

3. In connection with each process there should be careful study of the reactions depended upon for the final determination

of an atomic weight, looking especially to the possibility of the occurrence of secondary or subsidiary reactions.

4. Each process adopted should be as simple as possible, both in the nature of the chemical reaction or reactions and in the known liability to merely manipulative errors.

5. Each process should be carried out with, in some experiments larger, and in others smaller, quantities of material. But, on the whole, the quantities used should be kept within such limits as are most likely to admit of most accurate determinations being had under the conditions of the special process.

6. In the reactions depended upon only such other elements should be concerned as may be counted among those of which the atomic weights are already known with the nearest approach to exactness.

7. It is particularly desirable that, if possible, the atomic weight to be investigated shall be, by at least one process, compared directly with that of hydrogen, now almost universally taken as the basis for the whole list of the elements. It is remarkable for how very few of the elementary substances—not more than three or four—this direct comparison has been accurately made.

8. In the greater number of the processes available for atomic weight determinations the comparison with hydrogen must perforce be made indirectly. When this is the case, it is desirable that as few other elements as possible, the assumed atomic weights of which will have to be taken into account, shall be involved in each single reaction depended upon.

9. In selecting *different* processes to be applied to the determination of the atomic weight of a given element, in order that the results may check each other, it is desirable that, not the same, but as many different other elements as possible, shall be concerned in the several reactions, provided all such elements count amongst those of which the atomic weights may be considered in the first rank as to the accuracy with which they are known.

Means and Methods of Weighing Employed.

These were in the main the same as those which I had in former years used in determining the atomic weight of aluminum.

The balance chiefly used, made by Becker, was carefully cleaned, and all its parts adjusted, especially as to the position of

the centre of gravity for each load to be used. A second balance by the same maker, of larger size, capable of taking a load of a kilogram in each pan, was employed in weighing certain of the solutions experimented on, and was in like manner carefully adjusted and tested. All weighings were made by observation of the oscillations of the index on either side of the position of rest. A difference of weight of .0001 gram with the smaller balance, and .0002 gram with the larger instrument, was easily and distinctly observable with any load which the research required.

The same kilogram weight was made the basis of a comparison with all my other weights which had been before used in the same way. This had been compared at Washington with the "star kilogram" of the United States Coast Survey, the value of which is known in terms of the original "kilogram of the Archives" at Paris. All the smaller weights were carefully rechecked against this and against each other, and their real values ascertained as referred to a vacuum. The necessary determinations were made of the specific gravity of all materials and vessels which were to be weighed, and the barometer and thermometer were read at the time of each weighing, so that all weights recorded in this paper represent real values *in vacuo*. In order to reduce to a minimum errors due to varying deposition of hygroscopic moisture, vessels of like material, shape and size with those used to contain substances to be weighed were used as tare.

History and Mode of Purification of the Gold used in this Research.

Most of the metal needed was prepared by myself, with precautions presently to be mentioned; a part was obtained, as "proof gold," from the United States Mint at Philadelphia; another part from the United States Assay Office at New York; and a single specimen of English "trial plate" gold from the Royal Mint in London.

1. *Purification of Gold by the Author.*—It may fairly be concluded from the general history of the gold of commerce that the impurities most to be suspected, and most requiring special precautions for their removal, are silver and the metals of the platinum group. My preliminary experiments led me to believe that the greatest difficulty in the way of obtaining perfectly pure gold consists in getting rid of the last traces of silver, the chloride of this metal not being quite insoluble in a solution of auric chloride. For

the removal of silver I have chiefly depended upon evaporation of the gold solution with a little hydrobromic acid, followed by large dilution with water, and long-continued clearing by subsidence. As regards the platinum metals, my results agreed substantially with those of Hoffmann and Krüss,¹ but I have been inclined to lay some stress on reduction of the gold from its solution *with exclusion of light*, and on *fractional* reduction, using only the middle portion thrown down. I avoided altogether the use of ferrous salts as reducing agents, in view of the difficulty of preparing them in large quantity with assurance of their purity and the trouble of thoroughly washing the precipitated gold. For the final precipitation of the gold formic acid seemed to offer real advantages; its volatility admits of easily getting it free from any metallic contamination, and the reduction is more easily effected than with oxalic acid.

Starting with United States gold coin, it was first heated to bright redness in a muffle, as a precaution against the presence of any traces of mercury, and to remove any grease, etc., from the surface, and then dissolved in a mixture of pure hydrochloric and nitric acids in the right proportions. The solution was evaporated with excess of hydrochloric acid nearly to dryness, the auric chloride redissolved in a considerable quantity of water, and the solution allowed to settle for four or five days. The greater part of the clear liquid, drawn off with a syphon, and filtered through very fine siliceous sand,² was again evaporated nearly to dryness, adding towards the end a few drops of pure sulphuric acid, in case of the conceivable, though unlikely, presence of such traces of lead as this might reveal; much pure water was added, the solution again cleared by subsidence for several days, and the greater part of the clear liquid again drawn off and filtered. This solution was now rendered pretty strongly acid with hydrochloric acid, and fractionally precipitated by sulphurous acid (SO_2 was evolved from sodium sulphite), at as low a temperature as possible, and *in the dark*, putting aside the first and last portions of the metal thrown down, and reserving for further treatment the (largest) middle portion. The gold thus obtained was well washed with water, boiled with nitric acid alone, again washed, boiled with hydro-

¹ Ann. Chem. (Liebig) 238, 66.

² The sand was carefully purified beforehand by boiling with nitric and hydrochloric acid, thorough washing with water, and heating to redness in the air.

chloric acid alone, again washed, dried, and heated strongly with fused acid sulphate of potassium in a porcelain crucible, boiled with dilute hydrochloric acid, and then with water. The metal was redissolved in aqua regia, the solution evaporated nearly to dryness, with addition of pure hydrobromic acid towards the end, very largely diluted with water, and allowed to stand for two days, well protected from dust, before again syphoning off as much of the clear portion as could be safely removed without risk of disturbing the remainder at the bottom, using a conical precipitating jar with greatest diameter below, and filtering the liquid through siliceous sand as before. The evaporation with hydrobromic acid was repeated twice more, and the clear solution—allowed the last time to stand a month before being syphoned off and filtered—was then reduced, once with oxalic acid (neutralising the liquid with pure sodium hydroxide from the metal), once (after re-solution) with sulphurous acid, and once with formic acid, washing the reduced metal well each time before redissolving in aqua regia. In the first and second of these reductions a little of the metal first and last thrown down was rejected, and in the final reduction with formic acid the first portion precipitated, about one-fifth of the whole, was reserved for use, labelled A, *a*, the middle portion, about three-fifths, was labelled A, *b*, and the last portion, the remaining one-fifth, was also preserved for use, marked A, *c*, so that it might be seen whether any difference in the character of the metal could be detected in the atomic weight determinations. All of these fractions received a very thorough final washing with water.

Such part of the purified metal as was to be used in the preparation of gold compounds was not fused, but was heated in a glazed porcelain tube to moderate redness in a Sprengel vacuum. A small part of the metal used in the free state, and desired in compact form, was fused in a perfectly clean Beaufaye crucible with a little acid sulphate of potassium and borax, the button flattened, boiled with strong nitric and then strong hydrochloric acid, thoroughly washed with water, and, finally, heated in the Sprengel vacuum. Throughout the long process of purification, and especially towards its close, the most scrupulous care was taken to exclude dust, and to prevent grains of sand from the bottoms of beakers or any other impurities getting into the precipitated gold, upon which the acids used would not act, so as to obviate the risk of merely mechanical contamination, which, if

overlooked, might lead to that being weighed as part of the gold which was, in fact, foreign to it.

2. *Purification of "Proof Gold" obtained from the United States Mint at Philadelphia.*—I owed to the kindness of Mr. J. B. Eckfeldt, Chief Assayer to the Philadelphia Mint, a liberal supply of the "proof gold" used in checking the gold assays there made, and he furnished me the following statement of the manner in which this purest metal is prepared, under his directions: "The best cornets from the gold assays selected and dissolved in aqua regia. Solution evaporated, with additions of HCl, to nearly crystallisation, diluted largely with water, and allowed to stand for three or four weeks. About seven-eighths of the solution drawn off from the silver chloride, and passed through several thicknesses of various filters. Solution somewhat concentrated, and alcohol and potassium chloride added, allowed to stand for some time (precip. traces of platinum¹), and carefully filtered. Gold precipitated by addition of pure ferrous sulphate. Reduced gold washed repeatedly in boiling HCl, until washings show no iron, then well washed in pure water. Gold dissolved, and solution evaporated to crystallisation, with repeated additions of hydrobromic acid,² diluted, and again allowed to stand for some time; filtered. Through the solution was passed pure SO₂ until all the gold was reduced; washed. Gold again dissolved, evaporated with HCl, diluted, and oxalic acid added, and heated until all gold is down. Melted in white clay crucible with potassium chlorate and nitrate, afterwards with pure sodium carbonate and borax." Mr. Eckfeldt also informed me verbally that the proof gold thus purified is cast into a small bar in a perfectly clean and bright cast-iron mould; the bar is boiled in nitric acid, washed and dried, rolled between fine steel rolls quite free from grease, and the strip finally cleaned for use with hot hydrochloric and then nitric acid.

In a letter of later date he wrote, "In preparing the 'proof' I seldom make over 10 ounces in one lot; from 8 to 10 ounces is the usual amount. There is comparatively little trouble in making

¹ The platinum of South American native gold, and of scrap gold from dentists, is at the Philadelphia Mint separated solely by alloying with enough silver, and dissolving out the latter metal with nitric acid. The platinum dissolves with the silver.

² I had, many months before, independently adopted and used hydrobromic acid to remove traces of silver more effectually than by hydrochloric acid, when I learned from Mr. Eckfeldt that he had thus habitually employed it.

999.9 fine, but beyond that it is rather troublesome; and it seems that, with all the care, the final result is sometimes a little in doubt."

The fine gold received from the Philadelphia Mint is designated as B in this paper, in connection with the experiments in which it was used.

3. *Purification of "Proof Gold" obtained from the United States Assay Office at New York.*—Dr. H. G. Torrey, Chief Assayer in this office, was obliging enough to let me have several samples of his finest proof gold, used in checking the regular assays in his department. He informed me that this proof gold was independently prepared at New York, but was occasionally compared with that of the Philadelphia Mint. He furnished the following brief statement as to its preparation: "The process used in preparing the gold is to dissolve 'cornets' (or gold from assays) in nitro-hydrochloric acid, and after filtration precipitating by oxalic acid, and after thorough washing melting under borax. The operation is conducted with the utmost care throughout."

The gold from this source is designated as C in this paper.

4. *Gold from the "Trial Plate" of Fine Gold of the English Mint.*—Professor Roberts-Austen, Chemist to the Royal Mint, was so kind as to let me have a specimen of a few grams of gold cut from the trial plate of the pure metal prepared by him in 1873. In its preparation use was made of potassium chloride and alcohol to separate any platinum present in the original material, a long period of subsidence was allowed for the deposit of any silver chloride from the solution, and the whole process was applied on a large scale, resulting in the purification of some 70 ounces of fine gold, of which Professor Roberts-Austen himself has said: "I have not been able to prepare, or to obtain from any source, gold of greater purity, even in small quantities." It seems, however, that the apparent standard of this gold was slightly reduced in rolling, the finished plate being counted as 999.95 fine in comparison with the same gold before rolling. A memorandum given me by Professor Roberts-Austen states that this trial plate gold is 999.98 fine as compared with the purest gold obtained by Stas for the Belgian Mint.

This specimen of English trial plate gold is designated as D in the present paper.

All the samples of gold received from others—B, C, and D—

were, before using them, carefully boiled in nitric acid to remove any possible traces of silver or other metal derived from the shears used in cutting the plates. They were also previously well washed with ether, to remove any grease, and afterwards with pure water, and were finally heated to redness in the Sprengel vacuum.

It may be remarked, in advance, that I have not been able to trace any probable connection between the history of the several samples of gold used and the values obtained for the atomic weight of the metal. Within the limits of accuracy attained, the results appear to have been sensibly the same by each method for all the gold used. Nor is there apparent in the results of Krüss, or those of Thorpe and Laurie, any evidence of a difference fairly traceable to the nature of the metal employed by them.

A considerable part of the gold prepared by myself was, after having once served for a determination of the atomic weight, redissolved and reprecipitated, and was afterwards more than once used in subsequent determinations, and yet no sign was obtained of any resulting influence upon the later values of the atomic weight as obtained, evidence being thus furnished of the purity, not only of the gold itself, but of the reagents used to act upon it, so far as any contamination of the metal was concerned. It may therefore be concluded with reason that the gold used in these experiments was of uniform character, and uniformly free from any known impurities, to such an extent, at any rate, as to sensibly change the results obtained.

It is to be noted that the only known elements having higher atomic weights than that of gold are mercury, thallium, lead, bismuth, thorium, and uranium. The presence of any of these in the gold experimented on, even in traces too minute to weigh, is in a very high degree unlikely. The presence of any other element or elements than these would, for analogous compounds, tend to lower the value obtained for the atomic weight of gold; so that, in considering the chances of error due to the nature of the metal used as gold, we should be inclined to say that the risk was rather in the direction of too low than too high a result being reached. But, if the possibility be observed of compounds not analogous being erroneously compared, the contrary error will be seen to be possible. Thus, in case the composition of an auric haloid salt obtained from a given amount of metallic gold should be examined, if any unsuspected silver were present there would be required for

the same amount of the halogen three atoms of silver instead of one atom of gold, and, therefore, the apparent weight of gold as compared with that of the halogen would be increased instead of diminished, and a higher value obtained for the atomic weight sought.

General Precautions Observed in the Experiments for Determination of the Atomic Weight.

All the reagents used were prepared or purified by myself, and most carefully tested for any traces of such impurities as might reasonably be suspected, and as could affect their application to the purpose in view. Particular care was bestowed upon the examination of the distilled water, acids, and other materials used in large quantity. To remove organic matter from the water required, it was distilled from a small amount of potassium permanganate and sulphuric acid.

Scrupulous care to exclude atmospheric dust was observed. In the evaporation of some of the gold solutions the process was carried out in a glass bottle of considerably larger capacity than the volume of liquid to be treated, furnished with a well-ground glass stopper of special construction, as shown in figs. 1 and 2, the

FIG. 1.

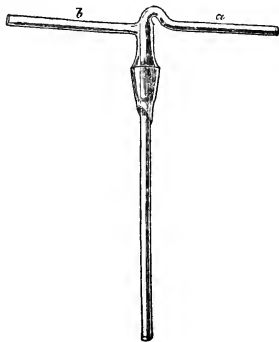


FIG. 2.



latter representing the stopper in place. Air, purified by passing through a red-hot tube, then through a solution of potassium permanganate and sulphuric acid, and dried by passing through

concentrated sulphuric acid and over solid potash, was introduced by the tube *a*, which went down to near the level of the liquid to be evaporated, while this air, charged with vapor of water from the liquid, was withdrawn through the tube *b* by means of a water-jet pump; the bottle was moderately heated by immersion to the greater part of its height in a water-bath.

In filtering the gold solutions no paper or other organic material was used, but fine white siliceous sand, previously boiled in nitric and hydrochloric acids, washed with water, and well ignited to burn off any organic matter, was substituted, supporting it on coarser sand and larger fragments of quartz, similarly purified, and the whole arranged so as to prevent the possibility of any sand grains being mechanically carried into the filtered liquid. Vessels of hard glass and Berlin porcelain were employed. Care was taken to work in a clean laboratory atmosphere, free from gases or vapors which might affect the materials dealt with.

First Series of Experiments.

A neutral solution of auric chloride was prepared by cautiously heating auric chloride, made, as suggested by Julius Thomsen, by the direct action of pure chlorine upon finely divided metallic gold, until such an amount of chlorine had been given off that on treating the residual material with moderately warm water, metallic gold only remained undissolved, which was then filtered off. This neutral solution having been rendered uniform by agitation, two approximately equal portions of it were weighed off, using, of course, stoppered vessels to prevent evaporation during the weighing. From one of these portions the gold was thrown down in the metallic state by pure sulphurous acid with the aid of heat, carefully collected, well washed, dried, ignited in a Sprengel vacuum, and weighed. To the other portion there was added the carefully prepared solution in a minimum of nitric acid of an accurately weighed quantity of pure silver, a little more than equivalent to the chlorine present, the liquid and precipitate digested together for a considerable time with gentle warming in a stoppered glass flask, well agitated from time to time, and the precipitate (of silver chloride, containing also the gold) filtered off upon siliceous sand, and thoroughly washed, avoiding throughout the decomposing influence of light. The clear filtrate was nearly neutralised with pure sodium hydroxide (from metallic sodium),

evaporated down to a small bulk, using the vessel represented in fig. 2 (p. 91), and finally the remaining silver was determined (with all the needful precautions of the silver assay) by means of a weighed quantity of a weak solution of pure hydrobromic acid standardised against pure silver. This mode of determining chlorine by means of silver and hydrobromic acid was suggested to me in a letter, of the 27th of January, 1887, with which I was favored by M. Stas,¹ who advocates it as the most exact process available. The pure silver required was prepared in the same way as that used in my experiments on the atomic weight of aluminum,² and was heated in the Sprengel vacuum to remove all occluded gas. The hydrobromic acid was prepared as directed by Stas in his published paper—"De la détermination du rapport proportionnel entre l'argent, les chlorures et les bromures."³

In reporting the results obtained, the quantity of gold stated is that actually weighed, but the quantity of silver corresponding thereto has, for the sake of simplicity, been given as that required for an exactly equal quantity of the auric chloride solution, while, as stated above, the quantity of liquid weighed off was very nearly, but not exactly, equal to that from which the gold was thrown down, the difference being allowed for in calculation.

With this explanation the results of the first series of experiments were as follows:

Experiment.	Character of gold used.	Gold, grams.	Silver required to precipitate Cl, grams.
I.	A, <i>a</i>	7.6075	12.4875
II.	A, <i>b</i>	8.4212	13.8280
III.	B	6.9407	11.3973
IV.	A, <i>c</i>	3.3682	5.5286
V.	C	2.8244	4.6371

In regard to conceivable sources of error connected with this method, it is to be observed that, in preparing the original auric chloride solution, if there should be any reaction between this gold salt and the water, leading to the formation of traces of hydrogen

¹ In this letter M. Stas says, "Je me permets de vous recommander l'emploi de l'acide bromhydrique pour la précipitation de l'argent resté dans un liquide après une double décomposition opérée à l'aide d'un *chlorure* et d'un sel d'argent. On réussit à condition que l'eau mère renferme un excès d'argent dont le poids est le triple du métal qui peut rester en solution à l'état de chlorure d'argent."

² Phil. Trans. 1880, p. 1020.

³ Mémoires de l'Acad. Royale des Sciences de Belgique, 43 (1882).

auri-chloride and precipitation of a little auric oxide or hydroxide, which might escape observation in admixture with the metallic gold left undissolved, the tendency would be to lower the atomic weight found for gold. If, by reaction between this residual metallic gold and the auric chloride solution, any traces of aurous chloride were produced and taken up by the solution of the higher chloride, the effect would be to raise the apparent value of the atomic weight.¹

If, in the reaction of the silver solution upon that of auric chloride, *partial* withdrawal of chlorine should lead to the formation of any traces of aurous chloride, precipitated along with the chloride of silver, and not afterwards decomposed during the digestion of the precipitate with the remaining solution, the resulting error would also be in the direction of too high an atomic weight. The probability of the last supposition is diminished by an excess of silver for the whole amount of chlorine present having been added at once. It is not very likely that any one of these defects actually belongs to the method and affects its results to a sensible extent. Of the three I should be more inclined to suspect the possibility of the second than either of the two others.

Second Series of Experiments.

A neutral solution of auric bromide was prepared by a like process to that used in making the auric chloride of the first series: acting upon pure metallic gold with pure bromine (prepared with the precautions recommended by Stas), evaporating the solution to dryness out of reach of dust, cautious heating of the residue, re-solution of auric bromide, and filtration from undissolved metallic gold.

Two nearly equal portions of the solution were accurately weighed off, and treated as described above: in one reducing the gold to the metallic state and determining its weight; treating the other with a small excess of silver in solution as nitrate, filtering off the precipitate, concentrating the filtrate with the precautions already described, and determining in it the excess of silver by means of hydrobromic acid.

Reducing the amounts of silver actually used to the corresponding quantities for portions of auric bromide solution exactly

¹ These two remarks apply, of course, also to Krüss's first series of experiments.

equal to those from which in each case the gold was obtained, the results in six experiments stood as follows :

Experiment.	Character of gold used.	Gold, grams.	Silver required to precipitate Br, grams.
I.	A, <i>b</i>	8.2345	13.5149
II.	A, <i>c</i>	7.6901	12.6251
III.	B	10.5233	17.2666
IV.	A, <i>a</i>	2.7498	4.5141
V.	C	3.5620	5.8471
VI.	A, <i>b</i>	3.9081	6.4129

In these experiments the sources of constant errors which suggest themselves as possible are essentially similar to those for the first series; but, if any such really exist, there is, of course, the likelihood of some difference being introduced by the substitution of bromine for chlorine. Hence the desirability of multiplying experiments in this modified form.

Third Series of Experiments.

For these experiments potassium auri-bromide was prepared with great care from an excess of metallic gold treated with bromine and potassium bromide, purified in accordance with Stas's suggestions, and the double salt five times recrystallised. The last crystallisation was conducted fractionally, in closed vessels, with special care to exclude dust, by gradual but pretty rapid cooling with agitation, and the earlier and later portions separated out were kept apart in after use.

For each atomic weight determination an unweighed quantity of this potassium auri-bromide was dissolved in water, the solution rendered uniform by agitation, and divided into two nearly equal parts, which were severally weighed with accuracy, and in one the gold reduced to metal as in the experiments of the first and second series, and in the other the total bromine precipitated by silver solution as before, the comparison being made once more between the weight of the gold and that of the silver equivalent to the bromine (in this case representing 4 atoms) existing in the double bromide.

Again stating the quantities of silver corresponding to portions of the auri-bromide solution exactly equal to those used in determining the gold, the following were the results obtained :

Experiment.	Character of gold used.	Fraction of crystallised auri-bromide used.	Gold, grams.	Silver required to precipitate Br, grams.
I.	A, <i>b</i>	First	5.7048	12.4851
II.	A, <i>b</i>	Second	7.9612	17.4193
III.	B	First	2.4455	5.3513
IV.	B	Second	4.1632	9.1153

Of the tendencies to constant error which may be imagined in connection with the experiments of the first two series, and which have been noticed above, the first may probably be considered as not applying to the method pursued in this third series, while the second and third might still be applicable. But the superior stability of the double salt constitutes an advantage in its favor, and, as it formed the chief material for the experiments of Krüss and of Thorpe and Laurie, a comparison with their results is desirable, the mode of treatment pursued by me in ascertaining the composition of the salt not having been quite the same as that used by these chemists.

Fourth Series of Experiments.

A weighed quantity of trimethyl-ammonium auri-chloride, $[N(CH_3)_3HAuCl_4]$, was decomposed by heating in the air, and the weight of the residual metallic gold determined. This trimethylamine salt was selected because the base is of simple and well established constitution, and may with reasonable probability be counted upon as obtainable in a state closely approaching purity, and because the gold salt is easily crystallised, possesses a considerable degree of stability, and contains approximately half its weight of gold, so as to offer the most favorable chance of determining with accuracy the ratio between the metal left behind and the sum of the remaining constituents driven off on ignition. Although its use in fixing the atomic weight of gold involves the atomic weights of three other elements—carbon, nitrogen, and chlorine—all three of these constants deserve to be ranked amongst those already known with the nearest approach to precision at present attainable.

In order to obtain pure trimethyl-ammonium chloride, the impure commercial salt, derived from the *vinasse* of beet-root sugar making, was used, first setting free and distilling off a considerable quantity of trimethylamine and condensing at about the right temperature, and subsequently purifying the product by

Hofmann's method of treatment with ethyl oxalate and renewed distillation. The purified trimethylamine was several times fractionally distilled, and the portion of correct and most constant boiling point finally neutralised with pure hydrochloric acid. The concentrated solution of trimethyl-ammonium chloride was now precipitated by a strong solution of auric chloride, the mother liquor decanted off, and the gold salt redissolved in hot water, and recrystallised several times. The bright yellow crystalline powder was dried, first over sulphuric acid and afterwards over phosphorus pentoxide, until it ceased to lose weight; towards the end of the drying the temperature of the vessel was raised to about 50° C. Preliminary experiments seemed to indicate the probable existence of this salt crystallised with a single molecule of water, but most of that prepared contained no constituent water, and it appeared easy to attain complete drying without any decomposition of the salt itself. Throughout its treatment the salt, which was not in any high degree hygroscopic, was well guarded from dust and from any possible decomposing effect of light.

The portion of the salt to be used in each experiment was contained in a small glass-stoppered weighing flask, which was removed just before it was needed from the phosphorus pentoxide desiccator, the stopper having been inserted; the flask was weighed, the greater part of its contents transferred quickly to a weighed porcelain crucible, the stopper at once replaced, and, the flask being again weighed, the quantity of gold salt taken from it was found by difference.

In order to avoid mechanical loss by spattering on igniting the crucible and its contents, the auri-chloride lying together at the bottom of the crucible was covered by a layer, nearly a centimetre deep, of clean, carefully purified, and just previously well-ignited siliceous sand, the weight of this sand being known by taking it from a weighing flask in which it had been cooled over phosphorus pentoxide, and noting the loss of weight of this flask. In applying heat to the crucible and its contents it was found necessary to heat gently for a long time, raising the temperature slowly, in order to prevent extensive charring at the bottom. Then, before the temperature had become too high, but after a considerable part of the volatile matter had been driven off, the sand was carefully stirred in with the remaining material so as to produce pretty

uniform mixture, in order that the gold might not undergo partial welding together at a high temperature, which might have led to wrapping up particles of carbon and their protection from combustion. In this operation a very small porcelain stirrer was used, as a platinum wire would have welded on and taken up some of the metallic gold; the weight of this stirrer was determined in advance, and checked after use. Finally, the contents of the crucible were submitted to very careful and prolonged heating to moderate redness, with free access of air and occasional cautious stirring, so as to burn away every trace of carbon. After cooling in a desiccator, the crucible and its remaining contents were weighed, giving the weight of the residual gold by subtraction of the weights of the crucible itself and the siliceous sand. As an additional safeguard against any particles of carbon left unburned escaping detection, the gold was afterwards dissolved out with aqua regia, and the white sand carefully looked over with a lens.

The results of five experiments thus conducted were as follows:

Experi- ment.	Character of gold used.	Character of gold salt used.	Salt ignited, grams.	Residual gold, grams.	Loss by ignition, grams.
I.	A, δ	Earlier crop of crystals	14.9072	—7.3754	= 7.5318
II.	A, δ	Middle “ “ “	15.5263	—7.6831	= 7.8432
III.	A, δ	Last “ “ “	10.4523	—5.1712	= 5.2811
IV.	C	Middle “ “ “	6.5912	—3.2603	= 3.3309
V.	C	Last “ “ “	5.5744	—2.7579	= 2.8165

In these experiments the most probable source of error may be fairly taken as arising from the presence of traces of methyl-ammonium or dimethyl-ammonium auri-chloride with the trimethyl-ammonium salt. I know of no direct evidence that any such impurity was present, and the absence of any such evidence in the results from the earlier as compared with the later crops of crystals rather tells against the supposition of its presence, but one cannot feel certain of its entire absence. If present, its effect would be to raise the atomic weight obtained for gold. It is also conceivable that there may have occurred volatilisation of gold to a minute extent as auric chloride, in accordance with the observation of Krüss that this salt may be sublimed in small quantity at moderate temperatures in a stream of chlorine; but, there being no such stream of chlorine in these experiments, and on the contrary the decomposing action of the hydrogen of the trimethylamine salt, this does not seem likely; the effect would, of course, be to

raise the atomic weight obtained for gold. Another possible cause of error might consist in imperfect drying of the gold salt used, but the constancy of weight attained on drying renders it unlikely that any other than extremely minute error should come of this, though not altogether excluding the possibility of its occurrence; its tendency would, of course, be to lower the atomic weight obtained. Any trouble from hygroscopic moisture on the surface of the porcelain crucible and sand was, I think, satisfactorily guarded against by the use of a corresponding tare crucible, and by more than one weighing after a near approach to the true figures had been obtained, the crucibles having meanwhile been restored to the desiccator and kept therein for some time. The precautions taken seemed to afford sufficient protection against any merely mechanical loss during the ignition.

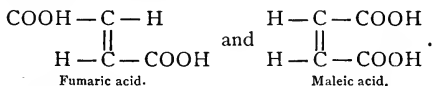
[To be continued.]

ON THE SYNTHESIS OF FUMARIC ACID.

(Preliminary Communication.)

BY E. H. KEISER.

Van't Hoff¹ has proposed the following stereometric formulas for fumaric and maleic acids:

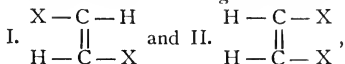


Johannes Wislicenus² has shown in a series of important papers that it is possible to determine experimentally the stereometric formulas of certain isomeric compounds. A consideration of the hypothesis put forward by him suggested the idea that it ought to be possible to prepare both fumaric and maleic acids synthetically from acetylene. In accordance with Van't Hoff and Wisli-

¹ Lagerung der Atome im Raume, p. 21.

² Räumliche Anordnung der Atome in organischen Molekülen. Ann. Chem. (Liebig) 246,

cenus's theory, the di-halogen additive compounds of acetylene can exist in two isomeric forms having the formulas



in which X represents any halogen atom. And further, compounds having the constitution represented by formula I are more stable than those having the structure represented by the second formula. Fumaric acid would then appear to be closely related to the halogen derivatives of the first class and maleic acid to those of the second.

It occurred to me that it might perhaps be of interest in this connection to start with acetylene and prepare, in the first place, two isomeric di-halogen additive compounds, and then endeavor to transform these into fumaric and maleic acid. The investigation is not yet completed, but one of the acids,—namely, fumaric acid—has been prepared in this way from acetylene.

Acetylene was prepared by the action of alcoholic potash upon ethylene bromide, and the purified gas was passed through a series of wash bottles containing crystals of iodine covered with a layer of absolute alcohol. After a time the iodine disappeared, and from the liquid two isomeric acetylene diiodides were separated. One of these compounds is a solid at ordinary temperatures, the other is a liquid. The solid diiodide is much more stable than the liquid variety. It does not decompose on standing, and can be sublimed without suffering change. On the other hand, the liquid diiodide undergoes decomposition when heated, and cannot be distilled with steam without being decomposed. These compounds have been prepared by Sabanejeff,¹ who has analysed them, and found them to have the composition represented by the formula $\text{C}_2\text{H}_2\text{I}_2$. No attempt was made by him to determine their constitution.

In accordance with the Van't Hoff hypothesis, the solid acetylene diiodide, which is much more stable than the liquid diiodide, would

have the constitution represented by the formula $\begin{array}{c} \text{I} - \text{C} - \text{H} \\ || \\ \text{H} - \text{C} - \text{I} \end{array}$ and

would, therefore, belong to the same general class of acetylene derivatives to which fumaric acid belongs. Now, experiment shows that this solid acetylene diiodide can be transformed into fumaric acid.

¹Ann. Chem. (Liebig) **178**, 118.

Nine grams of the acetylene diiodide crystals (m. p. 73°) were dissolved in alcohol, and 5 grams (2 molecules) of potassium cyanide added, and the solution was boiled for 36 hours in a flask with an inverted condenser. Caustic potash was thereupon added, and the boiling continued for two hours longer. On cooling the contents of the flask, a considerable quantity of needle-shaped crystals separated from the liquid. They were removed from the solution, and on examination proved to be the potassium salt of fumaric acid, which crystallises in the form of needles, insoluble in cold alcohol. More of the salt was obtained from the mother-liquor. The aqueous solution of the potassium salt was treated with silver nitrate, and a white precipitate consisting of the silver salt was obtained. The silver salt was purified by dissolving it in nitric acid and reprecipitating it by carefully neutralising the solution with ammonia. The silver salt of fumaric acid is characterised by its great insolubility in water and by the fact that when it is heated it deflagrates like gunpowder. Both of these properties were exhibited by the silver salt of the acid made by synthesis.

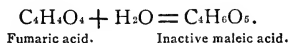
A quantitative determination of the percentage of silver gave the following result :

.2039 gram of the salt dried at 100° gave .1786 gram of AgCl = 65.97 per cent. Ag.

	Calculated for $\text{Ag}_2\text{C}_4\text{H}_2\text{O}_4$.	Found.
Ag	65.43	65.97

The free acid itself was recognised by its insolubility in water : it was precipitated from moderately concentrated solutions of its salt by the addition of strong acids. It will be analysed as soon as larger quantities of it have been obtained in pure condition.

In 1882 Sabanejeff¹ studied the action of potassium cyanide upon acetylene dibromide and obtained an acid having the formula $\text{C}_4\text{H}_6\text{O}_5$. It is probable that fumaric or maleic acid was first formed in his experiments, which afterwards, by the prolonged action of boiling caustic alkali, was converted into the acid $\text{C}_4\text{H}_6\text{O}_5$. It has been shown by Linnemann and Loydl² that when fumaric acid is heated with caustic alkalies it is gradually changed into an inactive maleic acid, thus :



¹Ann. Chem. (Liebig) **216**, 275.

²Ann. Chem. (Liebig) **192**, 80.

A more detailed study of the reactions which give rise to the formation of the two acetylene diiodides, as well as the attempt to prepare maleic acid from acetylene, is reserved for future work.

BRYN MAWR, PA., *February, 1890.*

A METHOD FOR THE DETECTION AND ESTIMATION OF PETROLEUM IN OIL OF TURPENTINE.

BY W. M. BURTON.

The use of the lighter boiling products of petroleum for the purpose of adulterating oil of turpentine is so well known to persons using these articles that little comment is necessary concerning the prevalence of this adulteration. Refined petroleum of the proper color and gravity can be mixed with turpentine in such proportions as to elude the common methods of detection. The gravity, color and odor of the mixture can be made identical with that of turpentine; whereas paint made from such material is not durable, but is liable to crack and peel off soon after its application. The pecuniary advantage to the unscrupulous dealer is also a great temptation to perpetrate this adulteration on the large scale. Allen, in his "Commercial Organic Analysis" (Vol. II, p. 441), describes a method for the detection of petroleum in turpentine. According to his description, the mixture is treated with strong sulphuric acid, when the terpenes are converted into polymers of a tarry consistency, while the petroleum is very slightly affected. This mixture is placed in a flask and steam blown through the mass, when a portion of the petroleum will be volatilised and can be collected in the usual way. This method requires considerable time and labor to obtain fair results, and, further, the yield of petroleum is far from being quantitative, leaving the operator in the dark as to the extent of the adulteration. The method which is here proposed is based upon the fact that petroleum is only slightly affected by fuming nitric acid in the cold, whereas turpentine is readily oxidised to various acids of the fatty and aromatic series, which are soluble in hot water. If, therefore, we treat a mixture of turpentine and refined petroleum with

cold fuming nitric acid, the terpenes will all be converted into acids readily-soluble in hot water, while the paraffins of the petroleum will remain almost entirely unaffected. These facts enable us to determine almost quantitatively the amount of petroleum contained in adulterated turpentine. The apparatus necessary for effecting this separation is very simple. A balloon flask of 750 cc. capacity is fitted with a two-hole cork stopper. Through one hole is inserted the tube of a glass-stoppered drop funnel having a capacity of 100 cc. The flask is also connected with an inverted condenser. About 300 cc. fuming nitric acid of sp. gr. 1.4 are placed in the flask, and 100 cc. of the turpentine to be tested are measured into the drop funnel. The flask is surrounded by cold water, and the turpentine is allowed to drop slowly into the nitric acid. As each drop strikes the acid, violent action takes place, with evolution of red fumes. It is well to shake the flask occasionally during the operation. When the turpentine has all passed into the flask, the apparatus is allowed to stand until all action is over. The contents of the flask are transferred to a large separating funnel and treated with successive portions of hot water. In this way all the products resulting from the action of the acid on the terpenes are removed, while any petroleum paraffins remain insoluble in water, and can readily be separated and measured.

Having procured some turpentine known to be free from petroleum, my assistant prepared mixtures of the pure turpentine with samples of refined petroleum of various boiling points. In order that my judgment in experimenting might not be influenced by knowing the quantities of material used, my assistant withheld from me the proportions employed in the mixtures. Ten mixtures were analysed, with the following results:

Pure turpentine used.	Petroleum used.	Boiling point of petroleum.	Petroleum found by method described.
65 cc.	35 cc.	about 250°	34.1 cc.
80	20	250	18.9
70	30	200	29.
80	20	200	18.5
90	10	200	8.9
80	20	100	17.8
70	30	100	28.4
85	15	100	13.5
80	20	75	17.9
70	30	75	28.

It will be noticed that the sum of the amounts of petroleum and turpentine used would be 100 cc. in each case, so that the number of cubic centimeters of petroleum found would also express the percentage of adulterant. It appears from the above results that the petroleum fractions which boil at about 250° are least affected by the fuming nitric acid, while the low-boiling fractions are affected the most. But in order to keep the specific gravity of the turpentine where it should be, the higher boiling petroleum fractions must be used in the adulteration—a fact which is favorable for the application of this method in the analysis of such mixtures.

CLEVELAND, OHIO, *December, 1889.*

ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH AND LEE K. FRANKEL.

The study of the electrolysis of the double cyanides of cadmium, copper and zinc enabled us to formulate conditions by which the separations of cadmium from zinc,¹ and cadmium from copper,² were possible, and in every particular satisfactory.

The ease with which cadmium was separated from zinc, and the very close results obtained with these metals, led us to apply the method to the separation of cadmium from cobalt and from nickel. Operating first with cadmium alone, we dissolved sufficient pure sulphate in water, so that 10 cc. of the solution would contain 0.1688 gram metallic cadmium. To this volume (10 cc.) were added four and one-half grams pure potassium cyanide, and the solution made up to 200 cc. with water. A current yielding 0.4 cc. OH gas per minute was allowed to act upon the same for a period of fourteen hours.

The deposited metal weighed 0.1686 gram, a difference of -0.11 per cent. from the theoretical. A second trial, with conditions precisely analogous to those just mentioned, gave 0.1690 gram cadmium, a difference of $+0.11$ per cent. from the theoretical.

¹ This Journal **11**, 352.

² J. Anal. Chem. **3**, 385.

Cadmium from Cobalt.

In the third experiment the conditions were the same as before, with this difference, that an equal amount of cobalt was also present in the solution. The result of the electrolysis gave 0.1689 gram cadmium, a difference of $+.05$ per cent. from the required.

The fourth experiment, similar in every way to the third, yielded 0.1689 gram cadmium, a difference of $+.05$ per cent. from the theoretical.

The cadmium was fully deposited on both occasions, and contained no cobalt.

Cadmium from Nickel.

Passing to the separation of cadmium from nickel, the results were so surprising that we give the same in detail, although negative in character:

	Cadmium present, in grams.	Nickel present.	Potassium cyanide, in grams.	Total dilution.	Strength of current in cc. OH gas per minute.	Cadmium found.
(1)	0.1688	100 per cent.	4½	200 cc.	0.3 cc.	0.1717
(2)	"	"	"	"	"	0.1702
(3)	"	"	"	"	"	0.1725
(4)	"	"	"	"	"	0.1750
(5)	"	"	"	"	"	0.1721
(6)	"	"	"	"	"	0.1737
(7)	0.1828	—	"	"	0.5	0.1827
(8)	"	75	"	"	"	0.1923
(9)	"	50	"	"	0.15	0.1841
(10)	"	"	"	"	0.5	0.1882
(11)	"	25	"	"	0.15	0.1854

The period of time during which the current acted in each of the above experiments was sixteen hours. Nickel was always found in the cadmium deposit, while in many cases the precipitation of the cadmium was incomplete. The conditions were varied, yet the results were wholly unsatisfactory. By greatly increasing the quantity of cyanide, we discovered that the cadmium precipitation was greatly retarded. Nickel, when alone and under the conditions given above, would not deposit with the strength of current used by us. This behavior is only another indication that if we would make electrolytic methods widely applicable, it is first necessary to extend the study of the action of the current to all

the salts possible, and investigate carefully the influence of each metal upon its associates under varying conditions.

From what we have thus far accomplished we find the electrolytic separation of cadmium from copper, from zinc, and from cobalt, in cyanide solution, all that could be expected from any method.

The cadmium deposits, in the experiments recorded in this paper, were always washed with boiling water; the drying was done upon the edge of a warm iron plate.

We have already called attention¹ to the fact that mercury is fully precipitated from its double cyanide by a comparatively feeble current, and that the separation of this metal from copper is possible so long as the quantity of the latter does not exceed 20 per cent. of the mercury present. More recently we have executed a series of experiments looking to the separation of mercury from zinc, nickel, and cobalt.

Mercury from Zinc.

The results with these metals are:

	Mercury present, in grams.	Zinc present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Mercury found.	Difference in per cent. from theoretical.
(1)	0.1715	—	4½	200 cc.	0.3 cc.	0.1717	+ 0.12 %
(2)	0.1715	—	"	"	"	0.1715	...
(3)	0.1715	100 %	"	"	0.25	0.1706	— 0.52
(4)	0.1715	"	"	"	"	0.1709	— 0.34

The time in each deposition was sixteen hours. From these figures the separation is possible. Mercury was not found with the zinc. In the following experiments it will be observed that the error is much less, and accordingly makes the method trustworthy and, from its accuracy, well suited for scientific as well as technical work :

	Mercury present, in grams.	Zinc present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Mercury found.	Difference in per cent. from theoretical.
(5)	0.2440	100 %	3	200 cc.	0.5 cc.	0.2435	— 0.20 %
(6)	"	"	3	"	"	0.2445	+ 0.20
(7)	"	"	4½	"	"	0.2441	+ 0.04
(8)	"	"	"	"	0.28	0.2445	+ 0.20
(9)	"	"	"	"	"	0.2431	+ 0.37
(10)	"	"	"	"	"	0.2454	+ 0.50

¹ This Journal 11, 264.

The time of precipitation, made at the ordinary temperature, amounted to sixteen hours. The mercury deposit was washed with hot water and dried upon a moderately warm plate.

Mercury from Nickel.

With these two metals the current was allowed to act for sixteen hours. The results are:

	Mercury present, in grams.	Nickel present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Mercury found.	Difference in per cent. from the theoretical.
(1)	0.2440	100 %	4½	200 cc.	0.4 cc.	0.2435	— 0.20 %
(2)	"	"	"	"	"	0.2432	— 0.32
(3)	"	"	"	"	"	0.2425	— 0.60

Mercury from Cobalt.

Our experience with these two metals was so unexpected that we append the poor as well as the good results, which were finally obtained:

	Mercury present, in grams.	Cobalt present.	KCN in grams.	Total dilution.	Current in cc. OH gas per minute.	Mercury found.	Difference in per- centage.
(1)	0.2440	100 %	4½	200 cc.	0.4 cc.	0.2386	— 2.21 %
(2)	"	"	"	"	0.4	0.2388	— 2.13
(3)	"	"	"	"	"	0.2364	— 3.11
(4)	"	"	"	"	"	0.2333	— 4.00
(5)	"	"	"	"	"	0.2366	— 3.02

The current acted for sixteen hours. Upon reducing the quantity of cobalt, and operating with the conditions in other respects the same as before (except in 11 and 13), we obtained:

	Mercury present.	Cobalt present.	KCN in grams.	Total dilution.	Current in cc. OH gas per minute.	Mercury found.	Difference in per- centage.
(6)	0.2440	75 %	4½	200 cc.	0.5 cc.	0.2353	— 3.56 %
(7)	"	"	"	"	0.86	0.2357	— 3.40
(8)	"	50	"	"	0.50	0.2385	— 2.25
(9)	"	"	"	"	"	0.2381	— 2.33
(10)	"	"	"	"	0.86	0.2321	— 4.80
(11)	"	25	3	"	0.5	0.2442	+ 0.09
(12)	"	"	4½	"	0.86	0.2342	— 4.01
(13)	"	12½	3	"	0.5	0.2445	+ 0.20

Inspection of these figures discloses the fact that nothing

approaching a separation of the two metals appears probable until in Experiment 11, where not only the quantity of cobalt is reduced, but also that of the potassium cyanide. The result is then surprisingly close (+.09 per cent.). This would seem rather to be due to the reduction of the quantity of cyanide, inasmuch as by its increase in Experiment 12 we again have a minus error of 4.01 per cent., and in Experiment 13, by reducing the quantity of cyanide to 3 grams, the result is satisfactory. As the quantity of cobalt in this instance was but half that in Experiment 12, the favorable result might be attributed to this, hence the following trials were made :

	Mercury present.	Cobalt present.	KCN in grams.	Total dilution.	Current in cc. OH gas per minute.	Mercury found.	Time of precipitation.	Difference in per- centage.
(14)	0.2250	—	3	200 cc.	0.5 cc	0.2250	16 hours.	—
(15)	"	25 %	"	"	"	0.2256	"	+ 0.26 %
(16)	"	50	"	"	"	0.2258	"	+ 0.35
(17)	"	75	"	"	"	0.2258	"	+ 0.35
(18)	"	100	2.2	"	"	0.2235	"	— 0.60

Cobalt was not found in the mercury deposit, nor mercury in the cobalt solution. Evidently the quantity of cyanide present exercises a marked influence upon the separation. Returning to the separation of cadmium from cobalt, it will be observed that there the amount of cyanide was $4\frac{1}{2}$ grams, while the quantity of metal was less, yet the separation proved satisfactory.

Silver from Copper.

It yet remains for us to record some experiments upon the separation of these two metals in cyanide solution. Reference to a former paper¹ will show that our attempts in this direction were at that time fruitless. It was after the successful separation of cadmium from copper in cyanide solution that we were impressed with the idea that the separation of silver from copper ought to occur, since silver deposits so readily, even when exposed to a very feeble current. In the communication to which we refer the current strength recorded was 1 cc. OH gas per minute. Since it was by carefully reducing this in other cases that we obtained good separations, we instituted a new series of experiments with silver and copper, acting upon the mixture with a much weaker current :

¹ This Journal 11, 264, and J. Anal. Chem. 3, 254.

	Silver present, in grams.	Copper present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Time in hours.	Silver found.	Difference in percentage.
(1)	0.1788	—	4½	200 cc.	0.10 cc.	16	0.1792	+ 0.22 %
(2)	"	—	"	"	0.23	"	0.1788	...
(3)	"	100 %	"	"	0.15	"	0.1788	...
(4)	"	"	"	"	0.30	"	0.1787	— 0.05
(5)	"	"	"	"	0.20	"	0.1784	— 0.20
(6)	"	"	"	"	"	"	0.1782	— 0.33
(7)	"	"	"	"	0.40	"	0.1783	— 0.28
(8)	"	"	"	"	0.15	"	0.1800	+ 0.60

We next dissolved 0.1732 gram pure metallic silver ; to its solution were added 100 per cent. copper and 4½ grams KCN. On electrolysing with a current of 0.15 cc. OH gas per minute, the resulting silver weighed 0.1725 gram. The latter contained no copper, nor could silver be detected in the copper solution.

A silver coin (ten cent piece) weighing 1.2236 gram was brought into solution and diluted to 100 cc. Of this solution two portions (25 cc. each) were electrolysed in the presence of 4½ grams KCN, with a current of 0.4 cc. OH gas per minute. The silver found was in

a. 89.64 per cent. b. 89.56 per cent.

Two silver determinations made with another coin gave

c. 89.44 per cent. d. 89.44 per cent.

A silver dime weighing 2.4507 grams—carefully cleaned with sodium hydroxide and alcohol—after solution in nitric acid and the expulsion of the excess of the latter, was electrolysed with a current of 0.7 cc. OH gas per minute in the presence of 7 grams KCN, and gave 2.1996 grams Ag = 89.79 per cent.

So far as we are aware this is the first electrolytic method which has been proposed for the separation of these metals.

Silver from Zinc.

No difficulty is experienced in separating these metals when in cyanide solution. Our results are as follows :

	Silver present, in grams.	Zinc present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Time in hours.	Silver found.	Difference in percentage.
(1)	0.1788	100 %	4½	200 cc.	0.23 cc.	16	0.1784	— 0.22 %
(2)	0.1788	"	"	"	0.40	"	0.1785	— 0.11
(3)	"	"	"	"	0.4	"	0.1779	— 0.50
(4)	"	"	"	"	0.4	"	0.1787	— 0.05

Applying the same procedure to the separation of

Silver from Nickel,

the results were good :

	Silver present, in grams.	Nickel present.	KCN in grams.	Total dilution.	Current in cc. OH gas per minute.	Time in hours.	Silver found.	Difference in percentage from theoretical.
(1)	0.1788	100%	4½	200 cc.	0.35 cc.	16	0.1785	— 0.16%
(2)	"	"	"	"	"	"	0.1778	— 0.50

Silver from Cobalt.

	Silver present, in grams.	Cobalt present.	KCN in grams.	Total dilution.	Strength of current in cc. OH gas per minute.	Time in hours.	Silver found.	Difference in percentage
(1)	0.1788	100%	4½	200 cc.	0.35 cc.	16	0.1728	...
(2)	0.1788	"	"	"	"	"	0.1747	...
(3)	0.1788	"	"	"	"	"	0.1758	...
(4)	"	"	"	"	"	"	0.1697	...

Recalling our experience in separating mercury from cobalt, we reduced the quantity of cyanide to three grams, and obtained :

(5)	0.1788	"	"	"	"	"	0.1794	+ 0.33%
(6)	"	"	"	"	"	"	0.1782	— 0.33

From experiments made to learn the action of the current upon solutions of cobalt in the presence of a great excess of potassium cyanide, we know that the higher cyanide of cobalt—the cobalticyanide—is produced, and may it not be this which in some manner combines with the last traces of mercury and silver to form double cyanides not decomposable by the current strength employed in our experiments, which, if increased, would not only throw out the mercury and silver, but also some cobalt? With cadmium the double compound, if formed, may be more readily broken up, hence the separation is easily made. By reducing the quantity of potassium cyanide with mercury and silver we afford no opportunity for the production of cobalticyanide in such quantity as to appreciably affect the deposition of the other metals.

Copper from Cadmium in the presence of Sulphuric Acid.

From the fact that it is possible to completely precipitate cadmium from the solution of its sulphate containing free sulphuric acid,¹ and as copper is also deposited under similar conditions, the separation of these metals when in this form would hardly be expected. The experiments given below show that notwithstand-

¹ Smith, this Journal 2, 42.

ing all this, their separation can be effected under the conditions indicated. The first results were negative.

Experiment.—10 cc. copper sulphate (=0.1975 gram metallic copper), 10 cc. cadmium sulphate (=0.1828 gram cadmium), 1 cc. H_2SO_4 (sp. gr. 1.09), with 150 cc. water, were electrolysed with a current generating 0.4 cc. oxyhydrogen gas per minute. The copper was fully precipitated, and with it considerable cadmium.

In a second series of three experiments, similar to that above, excepting that the current only gave 0.22 cc. OH gas per minute, the copper was entirely precipitated, but carried down some cadmium with it.

In a third series of three experiments, the sulphuric acid in each dish was increased to 5 cc. (sp. gr. 1.09). The current gave 0.22 cc. OH gas per minute. The copper was not completely precipitated, and cadmium had deposited upon the copper.

The fourth series was made up as follows:

1st Exp. 10 cc. copper sulphate = 0.1975 gram copper, 10 cc. cadmium sulphate = 0.1828 gram cadmium, 10 cc. H_2SO_4 (sp. gr. 1.09), 100 cc. water. Current = 0.3 cc. OH gas per minute. Time 12 hours. The copper deposit weighed 0.1968 gram.

2d Exp. Same as 1. Copper found 0.1964 gram.

3d Exp. 10 cc. cadmium sulphate = 0.1828 gram cadmium. 5 cc. H_2SO_4 (sp. gr. 1.09). 100 cc. water. Current as in 1 and 2. Cadmium was not precipitated.

In the fifth series of four experiments, a current generating 0.5 cc. OH gas per minute was employed. The quantity of acid was increased to 10 cc. and 15 cc. Cadmium separated together with the copper.

The sixth series included five experiments:

Exp. 1. 10 cc. copper sulphate = 0.1975 gram copper, 10 cc. cadmium sulphate = 0.1828 gram cadmium, 15 cc. H_2SO_4 (sp. gr. 1.09), 100 cc. water. Current = 0.20 cc. OH gas per minute. Copper found was 0.1969 gram.

Exp. 2. Same as 1, gave 0.1976 gram copper.

Exp. 3. Same as 1 and 2, except that the current generated 0.3 cc. OH gas per minute. Copper found was 0.1975 gram.

Exps. 4 and 5 were like 3. The copper deposited equaled 0.1969 gram and 0.1962 gram.

Tabulating the results we have:

	Copper required.	Copper found.	Difference in percentage.
I.	0.1975 gram.	0.1968 gram.	—0.35 per cent.
II.	"	0.1964	—0.55
III.	"	0.1969	—0.30
IV.	"	0.1976	+0.05
V.	"	0.1975	...
VI.	"	0.1969	—0.30
VII.	"	0.1962	—0.65

The filtrates from the deposited copper were examined for that metal. VII showed a trace of copper. Cadmium was not detected in the precipitated metal. Holding strictly to the conditions given above will enable any one to effect the separation of these two metals in the presence of sulphuric acid.

UNIVERSITY OF PENNSYLVANIA, *January 6, 1890.*

Contributions from the Chemical Laboratory of Harvard College.

LXVIII.—ON CHLORPYROMUCIC ACIDS.

BY HENRY B. HILL AND LOUIS L. JACKSON.

[Continued from page 51.]

χ -DICHLORPYROMUCIC ACID.

The formation of the ethyl ether of this acid by the decomposition of ethyl pyromucic tetrachloride has already been described. The ether was recrystallised from hot alcohol, and saponified by alcoholic sodic hydrate. On the addition of hydrochloric acid to the aqueous solution of the sodium salt, a sparingly soluble acid separates, which may easily be purified by recrystallisation from hot water.

The acid dried over sulphuric acid gave, on analysis, the following results:

I. 0.2196 gram substance gave 0.2672 gram CO_2 and 0.0237 gram H_2O .

II. 0.2212 gram substance gave 0.3492 gram AgCl .

	Calculated for $\text{C}_5\text{H}_2\text{Cl}_2\text{O}_3$.	I.	Found.	II.
C	33.15	33.18
H	1.10	1.20
Cl	39.22	39.03

γ -Dichlorpyromucic acid is readily soluble in ether or alcohol, and but sparingly soluble in cold water. In hot water it is freely soluble, and crystallises as the solution cools in long needles which melt at 197° – 198° . The acid readily sublimes unchanged below its melting point. Sodium amalgam slowly reduces it to pyromucic acid melting at 129° – 130° .

The solubility of the acid in water at 19.5° was determined in the usual manner. A solution of the acid saturated at 19.5° was boiled with baric carbonate, and the barium dissolved determined by precipitation with sulphuric acid.

I. 38.2670 grams solution saturated at 19.5° gave 0.0322 gram BaSO_4 .

II. 37.5125 grams solution saturated at 19.5° gave 0.0301 gram BaSO_4 .

The solution saturated at 19.5° therefore contained the following percentages of acid:

I.	II.
0.13	0.12

Baric γ -dichlorpyromucate, $\text{Ba}(\text{C}_5\text{HCl}_2\text{O}_3)_{2.4}\text{H}_2\text{O}$.—The barium salt may most readily be prepared by boiling the acid with baric carbonate. The salt is quite readily soluble in cold water, more soluble in hot water, and crystallises in columnar aggregations of prisms which contain four molecules of water. The crystallised salt is stable in the air, effloresces over sulphuric acid, and loses all its water at 100° .

I. 1.0471 gram air-dried salt lost at 100° 0.1285 gram H_2O .

II. 0.5464 gram air-dried salt gave 0.2235 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_5\text{HCl}_2\text{O}_3)_{2.4}\text{H}_2\text{O}$.	Found.	
		I.	II.
H_2O	12.66	12.27	...
Ba	24.07	...	24.05

0.4495 gram salt dried at 100° gave 0.2091 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_5\text{HCl}_2\text{O}_3)_2$.	Found.
Ba	27.56	27.35

The solubility of the salt in water at 19.5° was determined in the usual manner.

I. 11.1910 grams solution saturated at 19.5° gave 0.0820 gram BaSO_4 .

II. 8.6544 grams solution saturated at 19.5° gave 0.0644 gram BaSO_4 .

According to these determinations, the solution saturated at 20° contained the following percentages of anhydrous salt:

I.	II.
1.56	1.59

Calcic χ -dichloropyromucate, $\text{Ca}(\text{C}_6\text{HCl}_2\text{O}_3)_{2.4}\text{H}_2\text{O}$.—The calcium salt was prepared by boiling the acid with calcic carbonate. The filtered solution was then concentrated on the water-bath to a small volume, and the salt which separated was filtered out and washed with a little water. Since the salt appeared to be about as soluble in cold water as in hot, it was dissolved in water and the solution concentrated *in vacuo* over sulphuric acid. The salt which separated was then pressed dry with filter paper. It is quite readily soluble in water, and crystallises in prisms which contain four molecules of water. The crystallised salt is permanent in the air, effloresces slowly over sulphuric acid, and loses all its water at 117° .

I. 0.9075 gram air-dried salt lost at 117° 0.1380 gram H_2O .

II. 0.6080 gram air-dried salt gave 0.1746 gram CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_6\text{HCl}_2\text{O}_3)_{2.4}\text{H}_2\text{O}$.	I.	Found.	II.
H_2O	15.25	15.21		...
Ca	8.48	...		8.44

0.3377 gram salt dried at 117° gave 0.1152 gram CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_6\text{HCl}_2\text{O}_3)_2$.	Found.
Ca	10.00	10.02

The solubility of the salt in water at 19.5° was determined in the usual manner. The calcium was precipitated as oxalate and ignited with sulphuric acid.

I. 6.5743 grams solution saturated at 19.5° gave 0.1522 gram CaSO_4 .

II. 7.2115 grams solution saturated at 19.5° gave 0.1689 gram CaSO_4 .

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt:

I.	II.
6.81	6.89

Ethyl χ -dichlorpyromucate, $C_6HCl_2O_3C_2H_5$.—The process by which the ethyl ether was obtained has already been described. It is readily soluble in hot alcohol, sparingly soluble in cold alcohol, and crystallises in clustered prisms with rectangular truncations which melt at 72° – 73° . A sample of the ether melting at 72° – 73° was distilled under a pressure of 16 mm. and boiled constant at 122.5° , temperature of bath 170° – 175° . For analysis the ether was dried over sulphuric acid.

I. 0.2034 gram substance gave 0.2790 gram AgCl.

II. 0.2302 gram substance gave 0.3160 gram AgCl.

	Calculated for $C_6HCl_2O_3C_2H_5$.	Found.	
		I.	II.
Cl	33.98	33.91	33.94

In order to determine the constitution of this dichlorpyromucic acid we studied its oxidation products with aqueous bromine.

Action of Bromine and Water.

As it was desirable to compare the oxidation product obtained from this acid with that obtained from the $\beta\delta$ -dichlorpyromucic acid under the same conditions, the acid was suspended in five times its weight of water, somewhat more than four atoms of bromine added as rapidly as possible, and the solution boiled until the oil which was at first formed had nearly disappeared. The filtered solution was evaporated to dryness at a gentle heat, the crystalline residue dissolved in a little cold water, filtered, and again evaporated nearly to dryness. The acid which separated was readily soluble even in cold water, almost insoluble in hot chloroform or benzol. It was therefore pressed dry with filter paper and carefully extracted with hot benzol. The acid as thus prepared crystallised in microscopic crystals which melted at 188° – 189° , and moreover gave on analysis the percentage of chlorine required by monochlorfumarc acid.¹

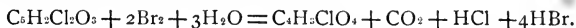
0.1441 gram substance dried over H_2SO_4 gave 0.1377 gram AgCl.

	Calculated for $C_4H_3ClO_4$.	Found.
Cl	23.59	23.62

The χ -dichlorpyromucic acid, like the $\beta\delta$ -dichlorpyromucic acid,

¹ Kauder, loc. cit.

therefore gives with aqueous bromine as the chief product chlor-fumaric acid according to the equation



Since the oxidation with bromine had shown with sufficient precision that one of the chlorine atoms of the χ -dichlorpyromucic acid occupied the δ position, we thought it unnecessary for our purposes to study also the action of nitric acid.

Action of Fuming Sulphuric Acid.

The two isomeric dibrompyromucic acids had shown marked differences in their behavior toward fuming sulphuric acid.¹ While the $\beta\gamma$ acid had rapidly been converted into the corresponding sulphonic acid, brommaleic acid in nearly theoretical quantity had been formed from the $\beta\delta$ -dibrompyromucic acid, and no trace of a sulphonic acid could be detected. Preliminary experiments proved that the $\beta\gamma$ - and $\beta\delta$ -dichlorpyromucic acids showed a similar difference in their behavior toward fuming sulphuric acid. While the formation of chlormaleic acid in the latter case could not definitely be proved, certainly no sulphonic had been formed, and it seemed to us of interest to study also the behavior of the third isomeric dichlorpyromucic acid under the same conditions. χ -Dichlorpyromucic acid dissolves readily in fuming sulphuric acid, and if care be taken to prevent any marked elevation of temperature no very essential decomposition ensues, although a slight effervescence is noticeable. After the solution of the acid in four times its weight of fuming sulphuric acid had stood for thirty-six hours, it was poured into a large amount of cold water, the solution cooled, and thoroughly extracted with ether. The ethereal extract left on evaporation a small quantity of a colorless oil which reduced silver oxide, and whose vapor vigorously attacked the eyes and nose. The amount of oil thus obtained was wholly insufficient for further study. On standing, it deposited a few clustered needles which probably were unaltered acid, although they may possibly have been the decomposition product subsequently described. From the aqueous solution the barium salt was prepared in the usual way, and, since the properties of the neutral salt were unfavorable to purification, it was converted into the acid salt, and this recrystallised from hot water. The acid salt was readily soluble in hot water,

¹ This Journal 10, 386 and 421; and Proc. Am. Acad., 23, 218.

more sparingly soluble in cold water, and crystallised in triclinic (?) prisms which effloresced on exposure to the air. It gave an excellent qualitative reaction for sulphur, and when dried over sulphuric acid¹ gave the percentage of barium required by the formula $\text{Ba}(\text{C}_5\text{HCl}_2\text{SO}_6)_2$.

0.3886 gram of the salt dried over sulphuric acid gave 0.1338 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_5\text{HCl}_2\text{SO}_6)_2$.	Found.
Ba	20.84	20.24

Baric χ -dichlorsulphopyromucate, $\text{BaC}_5\text{Cl}_2\text{SO}_6 \cdot 2\text{H}_2\text{O}$.—From the acid barium salt we prepared the neutral salt by neutralising its aqueous solution with baric carbonate. Since the hot saturated solution deposited little or nothing on cooling, it was evaporated *in vacuo* over sulphuric acid. The salt then crystallised in sheaves of prisms which appeared to be triclinic. It was permanent in the air, effloresced over sulphuric acid, and lost its water completely at 160° .

1.4159 gram of the air-dried salt lost at 160° 0.1277 gram H_2O .

	Calculated for $\text{BaC}_5\text{Cl}_2\text{SO}_6 \cdot 2\text{H}_2\text{O}$.	Found.
H_2O	8.33	9.02

0.5296 gram of the salt dried at 160° gave 0.3126 gram BaSO_4 .

	Calculated for $\text{BaC}_5\text{Cl}_2\text{SO}_6$.	Found.
Ba	34.59	34.69

The formation of a dichlorsulphopyromucic acid by the action of fuming sulphuric acid upon the χ -dichlorpyromucic acid is thus sufficiently established. The bromsulphopyromucic acids are so readily reduced in alkaline solution that we hoped to be able to prepare from this dichlorsulphopyromucic acid the corresponding sulphopyromucic acid, and thus establish the position of the two chlorine atoms. We soon found, however, that the chlorine was held with unusual persistence, and with the material at our disposal we have as yet been unable to reach decisive results.

¹The single determination of the water of crystallisation was unfortunately defective. It gave 13.34 per cent. of water in the salt dried by short exposure to the air, while a salt crystallising with $2\frac{1}{2}$ molecules of water should contain 13.70 per cent.

Decomposition by Hydrochloric Acid.

If the χ -dichlorpyromucic acid is heated with water in a sealed tube to 170° , no change is effected, but a reaction which we had in no way anticipated takes place if it is heated upon the water-bath in an open flask with concentrated hydrochloric acid. Carbonic acid is evolved, and in a short time the acid is completely decomposed with the formation of a neutral body which volatilises when the solution is boiled, and which can be extracted, although with difficulty, from the distillate, or from the original solution with ether. The ethereal solution left on evaporation a white crystalline solid which was sparingly soluble in water, readily soluble in cold chloroform or benzol, and but sparingly soluble in ligroin. When recrystallised from ligroin it formed long slender lustrous prisms, which melted at 52° – 53° , and sublimed rapidly at ordinary temperatures. It reduced argentic oxide on warming, and dissolved in aqueous alkalies, forming a yellow solution. The physical properties and the behavior of this substance at once recalled to our minds the crystalline body melting at 77° which Hill and Sanger¹ had obtained in small quantity from the by-products of the decomposition of pyromucic tetrabromide by alcoholic sodic hydrate. The formula of this body had been shown to be $C_4H_3BrO_2$, and an analysis of the new substance left no doubt of its similar composition.

0.1045 gram substance gave 0.1261 gram AgCl.

	Calculated for $C_4H_3ClO_2$.	Found.
Cl	29.95	29.84

This interesting body is probably formed according to the reaction



And since we found little difficulty in obtaining 40 per cent. of the yield which this equation demands, it will be possible to study it more in detail. Unfortunately, it was discovered so late in our work as to make it impossible to present the results of such a study in this paper. While it would be easy for us to venture a conjecture as to its structure, we prefer to await the results of a future investigation.

¹ Proc. Am. Acad. 21, 158.

TRICHLORPYROMUCIC ACID.

For the preparation of the trichlorpyromucic acid it was evidently most convenient to decompose with alkalis the tetrachloride of the δ -chlorpyromucic acid. It did not seem necessary, however, to prepare this tetrachloride in a pure condition, and indeed we first obtained the trichlorpyromucic acid from one of the earlier preparations of the ethyl pyromucic tetrachloride in which an unusually great spontaneous elevation of temperature had taken place through the rapid absorption of chlorine. For its preparation we heated the ethyl pyromucate to 145° , and passed in chlorine at this temperature until the gain in weight showed that one atom of hydrogen had been replaced by chlorine. We then allowed the temperature to fall to about 120° , and continued the chlorination to saturation. The total gain in weight then corresponded approximately to that required by the formation of the tetrachloride of the ethyl chlorpyromucate. On decomposing this product as usual with a cold concentrated alcoholic solution of sodic hydrate, the alcoholic solution filtered from the insoluble sodium salts contained, as in the previous cases, small quantities of liquid furfuran derivatives, but the amount was so minute that no separate study of them was made. The sodium salts dissolved in hot water gave with hydrochloric acid an impure trichlorpyromucic acid as a more or less colored oil, which solidified as the solution cooled. For the purification of the acid we have found it convenient to take advantage of the slight solubility of the ammonium salt in cold water. The crude acid was suspended in about thirty times its weight of water, ammoniac hydrate added in excess, and the hot solution treated with bone-black. The filtered solution deposits on cooling the greater part of the trichlorpyromucic acid as the ammonium salt from which the pure acid can readily be obtained. The small amount of trichlorpyromucic acid remaining in the ammoniacal solution may be recovered, although at the expense of considerable trouble, by precipitation with calcic chloride and repeated recrystallisation from water and dilute alcohol of the acid obtained from the insoluble calcium salt.

The yield of pure trichlorpyromucic acid was far from satisfactory, as we could obtain only 30 per cent. of the weight of the ethyl pyromucate taken, but 15 per cent. of the theoretical amount.

For analysis the acid was dried over sulphuric acid.

I. 0.3214 gram substance gave 0.3248 gram CO_2 and 0.0211 gram H_2O .

II. 0.2107 gram substance gave 0.4192 gram AgCl .

III. 0.2135 gram substance gave 0.4255 gram AgCl .

	Calculated for $\text{C}_6\text{HCl}_3\text{O}_3$.	I.	Found. II.	III.
C	27.85	27.56
H	0.46	0.73
Cl	49.43	...	49.19	49.27

Trichlorpyromucic acid is readily soluble in alcohol or ether, quite readily soluble in boiling benzol, and but sparingly soluble in cold benzol. Hot water dissolves it but sparingly, and as the solution cools, most of the acid is deposited in microscopic needles which melt at 172° – 173° . This melting point was so much below that which we had been led to expect from analogy to the known acid containing bromine that we felt some doubt of its correctness, more especially since the crude acid was so far from pure. A sample of the acid melting at 172° – 173° was therefore recrystallised twice from water and then three times from benzol, without perceptibly changing the melting point. The acid was then converted into the calcium salt, and this separated by crystallisation into three successive fractions. The acid from these three fractions melted simultaneously and sharply at 172° – 173° . Finally, the ethyl ether was made, and the acid prepared from the repeatedly recrystallised pure ether melted at the same point.

The solubility of the acid in water at 19.5° was determined by boiling with baric carbonate a weighed quantity of a solution of the acid saturated at that temperature, and determining the barium dissolved as sulphate.

I. 49.1742 grams solution saturated at 19.5° gave 0.0344 gram BaSO_4 .

II. 47.0228 grams solution saturated at 19.5° gave 0.0331 gram BaSO_4 .

The solution saturated at 19.5° therefore contained the following percentages of acid :

I.	II.
0.13	0.13

Baric trichlorpyromucate, $\text{Ba}(\text{C}_6\text{Cl}_3\text{O}_3)_{2.4}\text{H}_2\text{O}$.—The barium salt was prepared by precipitating a dilute solution of the am-

monium salt with baric chloride, and recrystallising the sparingly soluble salt thus thrown down from hot water. The salt proved to be but sparingly soluble even in hot water, and still less soluble in cold water. It separates from a hot concentrated solution in needles which apparently contain four molecules of water. The salt is permanent in the air, but loses three molecules of its crystal water over sulphuric acid. When dried at 120° it still retains a half-molecule of water, which cannot be expelled without essential decomposition.

I. 0.6847 gram air-dried salt gave 0.2511 gram BaSO_4 .

II. 0.6205 gram air-dried salt gave 0.2273 gram BaSO_4 .

III. 0.5672 gram air-dried salt gave 0.2076 gram BaSO_4 .

IV. 1.3625 gram air-dried salt lost over H_2SO_4 0.1148 gram H_2O , and at 120° 0.1338 gram H_2O .

V. 1.1645 gram air-dried salt lost over H_2SO_4 0.1003 gram H_2O , and at 100° 0.1124 gram H_2O .

VI. 1.3000 gram air-dried salt lost over H_2SO_4 0.1124 gram H_2O and at 100° 0.1256 gram H_2O .

Calculated for $\text{Ba}(\text{C}_6\text{Cl}_3\text{O}_3)_2 \cdot 4\text{H}_2\text{O}$.		Found.					
		I.	II.	III.	IV.	V.	VI.
Ba	21.47	21.56	21.54	21.52
$3\text{H}_2\text{O}$	8.46	8.43	8.61	8.65
$3\frac{1}{2}\text{H}_2\text{O}$	9.87	9.83	9.65	9.66

I. 0.7484 gram substance dried at 120° gave 0.3038 gram BaSO_4 .

II. 0.6247 gram substance dried at 100° gave 0.2521 gram BaSO_4 .

III. 0.6497 gram substance dried at 100° gave 0.2634 gram BaSO_4 .

Calculated for $\text{Ba}(\text{C}_6\text{Cl}_3\text{O}_3)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$.		Found.	
		I.	III.
Ba	23.83	23.86	23.72
			23.84

The solubility of the salt in water at 19.5° was determined in the usual way.

I. 41.4499 grams solution saturated at 19.5° gave 0.0470 gram BaSO_4 .

II. 44.9822 grams solution saturated at 19.5° gave 0.0500 gram BaSO_4 .

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt:

I.	II.
0.27	0.27

Calcic trichlorpyromucate, $\text{Ca}(\text{C}_5\text{Cl}_3\text{O}_3)_{2.4}\text{H}_2\text{O}$.—The calcium salt was prepared by precipitating a dilute solution of the ammonium salt with calcic chloride. The precipitated salt was then crystallised from hot water, and proved to be sparingly soluble in hot water, still less soluble in cold water, and separated from a hot solution in irregular aggregations of small leafy plates.

The salt is permanent in the air, effloresces over sulphuric acid, and loses all its water at 110° .

I. 1.3008 gram air-dried salt lost at 110° 0.1697 gram H_2O .

II. 1.8389 gram air-dried salt lost at 110° 0.2417 gram H_2O .

	Calculated for $(\text{C}_5\text{Cl}_3\text{O}_3)_{2.4}\text{Ca} \cdot 4\text{H}_2\text{O}$.	I.	Found.	II.
H_2O	13.30	13.05		13.14

I. 0.6399 gram salt dried at 110° gave 0.1855 gram CaSO_4 .

II. 0.6974 gram salt dried at 110° gave 0.2019 gram CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_5\text{Cl}_3\text{O}_3)_{2.4}$.	I.	Found.	II.
Ca	8.53	8.53		8.51

The solubility of the salt in water at 19.5° was determined in the usual manner. The calcium was precipitated as oxalate, and the oxalate ignited with sulphuric acid.

I. 18.1457 grams solution saturated at 19.5° gave 0.0342 gram CaSO_4 .

II. 14.6806 grams solution saturated at 19.5° gave 0.0265 gram CaSO_4 .

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt:

I.	II.
0.65	0.62

Potassic trichlorpyromucate, $\text{KC}_5\text{Cl}_3\text{O}_3$.—The potassium salt was prepared by boiling the acid with a slight excess of potassic carbonate. The solution was then concentrated until the salt began to separate, and on cooling it solidified to a mass of crystals, which were filtered off on the pump and pressed dry with filter paper. The salt is readily soluble even in cold water, and separates from a hot concentrated solution in sheaves of fine needles, which lose nothing in weight when heated to 120° . Analyses of the salt dried at this temperature proved it to be anhydrous.

I. 0.5338 gram salt dried at 120° gave 0.1851 gram K_2SO_4 .

II. 0.4425 gram salt dried at 120° gave 0.1532 gram K_2SO_4 .

	Calculated for $\text{KC}_5\text{Cl}_3\text{O}_3$.	I.	Found.	II.
K	15.42	15.57		15.54

Argentich trichlorpyromucate, $\text{AgC}_6\text{Cl}_3\text{O}_3$.—The silver salt may best be prepared by precipitating a hot solution of the calcium salt with argentic nitrate. For analysis the precipitated salt was well washed, and then recrystallised from hot water. It is sparingly soluble even in hot water, less soluble in cold water, and crystallises from a hot concentrated solution in moss-like aggregations of fine needles.

The air-dried salt gave on analysis much too low a percentage of silver, and although the sample analysed was free from calcium salt and free acid, it failed to give perfectly satisfactory results even when dried *in vacuo* over sulphuric acid or at 100° .

I. 0.5142 gram salt dried *in vacuo* over H_2SO_4 gave 0.2254 gram AgCl .

II. 0.4545 gram salt dried at 100° gave 0.1998 gram AgCl .

	Calculated for $\text{C}_6\text{Cl}_3\text{O}_3\text{Ag}$.	I.	Found.	II.
Ag	33.48	33.00		33.10

Ethyl trichlorpyromucate, $\text{C}_6\text{Cl}_3\text{O}_3\text{C}_2\text{H}_5$.—The ethyl ether was prepared in the usual manner, by warming an alcoholic solution of the acid with concentrated sulphuric acid. 5 parts of the acid, 10 parts of absolute alcohol, and 5 parts of concentrated sulphuric acid (sp. gr. 1.84) were heated together for three hours at 100° . The ether was then precipitated with water, washed with warm dilute sodic carbonate, and finally with water. The ether is readily soluble in hot alcohol, more sparingly in cold alcohol, and crystallises in flat prisms which melt at 62° – 63° .

I. 0.2142 gram substance dried over H_2SO_4 gave 0.3793 gram AgCl .

II. 0.2536 gram substance dried over H_2SO_4 gave 0.4476 gram AgCl .

	Calculated for $\text{C}_6\text{Cl}_3\text{O}_3\text{C}_2\text{H}_5$.	I.	Found.	II.
Cl	43.74	43.77		43.64

Trichlorpyromucamide, $\text{C}_6\text{Cl}_3\text{O}_2\text{NH}_2$.—Concentrated aqueous ammonia attacks the trichlorpyromucic ether but slightly at ordinary temperatures. Even after three hours' heating in a sealed tube at 100° most of the ether was found to be unaltered, and we were obliged to prepare the amide from the acid chloride by the action of solid ammoniac carbonate. The amide is but spar-

ingly soluble even in hot water, and crystallises in long slender needles which melt at 160° – 161° .

0.3804 gram substance dried over H_2SO_4 gave 23.2 cc. moist N at 21° under a pressure of 765 mm.

	Calculated for $\text{C}_5\text{Cl}_3\text{O}_2\text{NH}_2$.	Found.
N	6.53	6.95

Although there could be no doubt as to the constitution of the trichlorpyromucic acid, it seemed better for the sake of completeness to study its behavior with oxidising agents.

Action of Bromine and Water.

Trichlorpyromucic acid was suspended in ten times its weight of cold water, and a little more than one molecule of bromine was added. Carbonic dioxide was evolved and the color of the bromine rapidly disappeared. When the reaction had been completed, a white insoluble substance remained, which was removed by filtration and washed with a dilute solution of sodic carbonate. The alkaline solution gave on acidification a copious precipitate of unaltered trichlorpyromucic acid, whose identity was established by the melting point 172° – 173° . The substance which remained undissolved by the alkaline solution had the characteristic odor of the tetrabromfurfuran, and crystallised from hot alcohol in irregular plates which melted at 75° – 76° . Analysis showed this substance to be a trichlorbromfurfuran.

I. 0.1749 gram substance dried over H_2SO_4 gave 0.4269 gram AgCl and AgBr .

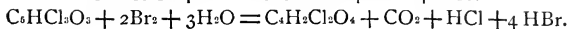
II. 0.1411 gram substance dried over H_2SO_4 gave 0.3447 gram AgCl and AgBr .

	Calculated for $\text{C}_4\text{Cl}_3\text{BrO}$.	I.	Found.	II.
$\text{Cl}_3 + \text{Br}$	74.45	73.60		73.67

The strongly acid filtrate from the trichlorbromfurfuran and unaltered trichlorpyromucic acid yielded on extraction with ether a crystalline acid which was readily soluble in water. The amount of this acid was too small for analysis, but it was easily identified as dichlormaleic acid by the melting point of its anhydride, 119° – 120° .¹

The reaction had therefore taken place in accordance with the following equations:

¹ Ciamician and Silber, *loc. cit.*



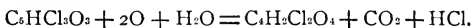
Action of Nitric Acid.

Trichlorpyromucic acid is but slowly attacked by nitric acid, and prolonged heating with moderately strong nitric acid is needed for complete oxidation. Even after heating the acid for six hours with six times its weight of nitric acid (sp. gr. 1.42) diluted with an equal weight of water, a portion of the trichlorpyromucic acid escaped oxidation. Carbonic dioxide was slowly given off, and a small quantity of an insoluble oil was formed, which had a peculiar penetrating odor not unlike that of substituted furfuran derivatives. Its quantity was too small to admit of its identification. In solution we were able to find nothing but dichlormaleic acid, which we purified through the barium salt and identified by the melting point of its anhydride and by analysis.

0.1997 gram substance dried over H_2SO_4 gave 0.3086 gram AgCl .

	Calculated for $\text{C}_4\text{H}_2\text{Cl}_2\text{O}_4$.	Found.
Cl	38.38	38.20

The reaction had therefore taken place in accordance with the following equation:



We have also prepared several other trisubstituted pyromucic acids, which may conveniently be described here.

$\beta\gamma$ -DICHLOR- δ -BROMPYROMUCIC ACID.

Hill and Sanger¹ found that $\beta\gamma$ -dibrompyromucic acid was easily converted into tribrompyromucic acid by the action of bromine at ordinary temperatures.

If $\beta\gamma$ -dichlorpyromucic acid is exposed to the vapors of bromine at ordinary temperatures, bromine is rapidly absorbed, hydrobromic acid is evolved, and the gain in weight approaches that required by the displacement of hydrogen by bromine. The product was treated with small quantities of boiling water to remove unaltered dichlorpyromucic acid, and then recrystallised from

¹ Proc. Am. Acad. 21, 172.

dilute alcohol and finally from water. The acid is readily soluble in alcohol or ether, dissolves freely in boiling benzol, more sparingly in cold benzol. Even in boiling water it is very sparingly soluble. It crystallises in short clustered prisms which melt at 185° – 186° .

0.3189 gram substance dried over H_2SO_4 gave 0.5817 gram AgCl and AgBr .

	Calculated for $\text{C}_5\text{HCl}_2\text{BrO}_3$.	Found.
$\text{Cl} + \text{Br}$	58.08	57.99

$\beta\gamma$ -DIBROM- δ -CHLORPYROMUCIC ACID.

This acid we made by treating the ethyl $\beta\gamma$ -dibrompyromucate with chlorine and decomposing the product with alcoholic sodic hydrate. On acidifying the aqueous solution of the sodium salts thus obtained, a crystalline acid was precipitated, which after one recrystallisation from dilute alcohol melted at 192° – 193° . After recrystallisation from benzol the melting point rose to 193° – 194° . The acid was readily soluble in alcohol, ether, or hot benzol, sparingly soluble in cold benzol, or even in boiling water.

0.2315 gram substance dried over H_2SO_4 gave 0.3960 gram AgCl and AgBr .

	Calculated for $\text{C}_5\text{HClBr}_2\text{O}_3$.	Found.
$\text{Cl} + \text{Br}_2$	64.19	64.37

We have attempted to prepare these acids also by the decomposition with alcoholic sodic hydrate of products formed by the addition of bromine to δ -chlorpyromucic acid and of chlorine to ethyl δ -brompyromucate. Although we readily prepared in this way trisubstituted acids, the products in neither case were homogeneous, tribrom- or trichlorpyromucic acids being formed together with the acid containing both halogens.

$\beta\gamma$ -DICHLOR- δ -NITROPYROMUCIC ACID.

Hill and Palmer¹ have shown that $\beta\gamma$ -dibrompyromucic acid is easily converted into a sulphonic acid by means of sulphuric acid, and that the sulpho group in this acid may readily be replaced by the nitro group. $\beta\gamma$ -dichlorpyromucic acid was dissolved in fuming sulphuric acid, and the barium salt of the sulphonic acid isolated in the usual way. Since a more complete study of the

¹ This Journal **10**, 386, 390; and Proc. Am. Acad. **23**, 201, 205.

salt did not fall within the plan of our work, we precipitated the barium exactly with sulphuric acid, and evaporated the dilute solution of the acid first at 100° and afterwards *in vacuo* over sulphuric acid. The crystalline, somewhat deliquescent acid thus obtained was dissolved in several times its weight of fuming nitric acid, to which half its volume of concentrated sulphuric acid had been added. After the action was finished, the nitric acid was partially expelled, the residue diluted with water and extracted with ether. The ether was then shaken with a dilute solution of sodic carbonate, and the acid precipitated from this alkaline solution by the addition of hydrochloric acid. The ethereal solution proved to contain no substance which invited farther investigation.

The $\beta\gamma$ -dichlor- δ -nitropyromucic acid is readily soluble in alcohol, ether, or hot benzol. Hot water dissolves it freely, and on cooling, the greater part of the acid is deposited in flattened leafy prisms which melt at 189° – 190° .

0.2168 gram substance dried over H_2SO_4 gave 0.2756 gram AgCl .

	Calculated for $\text{C}_6\text{HCl}_2\text{NO}_3$.	Found.
Cl	31.42	31.42

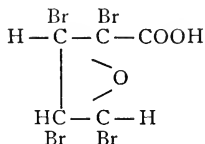
We have as yet made no further study of this acid.

THEORETICAL CONSIDERATIONS.

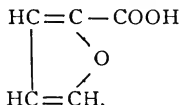
The acids melting at 168° – 169° and 155° – 156° , which in the preceding pages we have called the $\beta\gamma$ and $\beta\delta$ dichlorpyromucic acids, are without doubt identical in structure with the two dibrompyromucic acids described by Hill and Sanger.¹ Their physical properties and the solubility of their salts show their close relationship to these bromine derivatives, while the products formed from them by oxidation conclusively prove that they are structurally isomeric, and that the chlorine atoms occupy the same relative position that the bromine atoms hold in the dibrompyromucic acids. On reduction these two acids both yield the same chlorpyromucic acid, which in its turn closely resembles the β -brompyromucic acid in its physical properties, although its melting point, 145° – 146° , is comparatively high. It is to be noted, however, that the $\beta\gamma$ -dichlorpyromucic acid alone is formed by the action of alkalis

¹ Proc. Am. Acad., 21, 137.

upon the ethyl pyromucic tetrachloride, while the two isomeric dibromopyromucic acids are simultaneously formed under similar conditions. This simultaneous formation of the two structurally isomeric acids from pyromucic tetrabromide to which the formula



may be assigned, led Hill and Sanger¹ to the conclusion that these acids must have their bromine atoms in the $\beta\gamma$ and $\beta\delta$ positions respectively, and that pyromucic acid itself probably had the formula

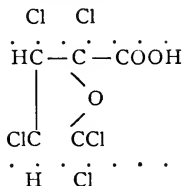


The structure of the $\beta\gamma$ and $\beta\delta$ dichloropyromucic acids seems to us to be thus sufficiently established.

As to the third isomeric form, which for the present we have called the χ -dichloropyromucic acid, since it gives chlorfumaric acid by oxidation, it is evident that it must either have its chlorine atoms in the γ and δ positions, or that it must be a geometrically isomeric form of the $\beta\delta$ acid. Unfortunately, we have been able to obtain as yet no evidence which conclusively proves either view to be correct. A dichloropyromucic acid having its chlorine atoms in the γ and δ positions could not well be formed from ethyl pyromucic tetrachloride by the simple loss of hydrochloric acid. Tönnies² had shown that δ -bromopyromucic acid could be formed by the action of heat upon pyromucic tetrabromide, when bromine must be eliminated as well as hydrobromic acid. Since we had noticed that hydrochloric acid invariably was evolved in the preparation of ethyl pyromucic tetrachloride, it seemed to us not improbable that the χ -dichloropyromucic acid was in fact the $\gamma\delta$ acid which had been formed in a similar way from the tetrachloride of the δ -chloropyromucic ether necessarily contained in the crude product.

¹ Ber. d. chem. Ges. **11**, 1088.

² Proc. Am. Acad. **11**, 182.



We found, however, that no χ -dichlorpyromucic acid was formed on heating ethyl δ -chlorpyromucic tetrachloride, and that our product in this case contained the $\beta\delta$ acid alone, so that the molecule of chlorine, which had been eliminated in the reaction, had taken its chlorine atoms from the γ and δ positions. We hoped also to get further evidence as to the structure of the χ -dichlorpyromucic acid by reducing it to a chlorpyromucic acid, or by substituting the chlorine of the χ -dichlorsulphopyromucic acid by hydrogen; but in neither case have we yet succeeded in obtaining well characterised products.

While it seems to us probable that the χ -dichlorpyromucic acid is geometrically isomeric with the $\beta\delta$ acid, we have as yet been unable to convert one acid into the other. Both acids volatilise unchanged when heated, and the ordinary reagents which usually effect conversion in such cases have failed to bring about any perceptible isomerisation. While lack of material has to a great degree limited our work with the χ acid, we have studied the behavior of the $\beta\delta$ acid under a variety of conditions, with purely negative results. If the two acids are in fact geometrically isomeric, the simultaneous appearance of both forms in the distillation of ethyl pyromucic tetrachloride with the escape of large quantities of hydrochloric acid shows that the conversion of one acid into the other is effected with difficulty, while the formation of the $\beta\delta$ acid alone from the ethyl δ -chlorpyromucic tetrachloride under similar conditions is especially worthy of note. Since pyromucic acid apparently contained two pairs of carbon atoms doubly tied, the existence of geometrically isomeric forms of its derivatives seemed at the outset more than probable, and during the progress of the investigations which for many years have been carried on in this laboratory, careful search had been made for such bodies, but hitherto only the two isomeric dibromfurfuran tetrabromides of Hill and Hartshorn¹ had been discovered. Since the discovery of

¹ Ber. d. chem. Ges, 18, 450.

the χ -dichloropyromucic acid, which we made toward the close of our work, we have attempted to prepare the corresponding bromine derivative, but as yet without success. The isolation of the body $C_4H_3BrO_2$, which Hill and Sanger¹ found among the products of the decomposition of pyromucic tetrabromide by alkalies, certainly is an indication of the previous existence of such an acid, although it is by no means clear in what stage of the process the decomposition of the acid was effected, nor how the decomposition product itself escaped further alteration. Any detailed consideration of the geometrical structure of pyromucic acid we feel obliged to postpone until more facts bearing upon the question are at our disposal.

REVIEWS AND REPORTS.

OSMOTIC PRESSURE AND THE DETERMINATION OF MOLECULAR WEIGHTS.

Within recent years it has become more and more apparent that an intimate connection exists between the stoichiometrical composition of a solution and its physical behavior. While earlier efforts towards proving this assumption were unsuccessful, chiefly because the experimental material was almost wholly confined to aqueous solutions of salts, which offer peculiar obstacles to such an investigation, F. Raoult's² patient researches upon organic substances in more varied solutions have enabled him to formulate accurately the long-expected laws, and to put the chemical world under lasting obligation for new methods for determining molecular weights under very favorable conditions. Raoult's law would read, in its most general form: In dilute solutions the depressions of the vapor tension and of the freezing point of the solvent vary directly with the ratio between the numbers of molecules of solvent and of substance dissolved in the mixture. Provided there be no chemical action involved in the process of solution, this relation is entirely independent of the nature of the substances.

Within the ordinary range of conditions, the *freezing point* of a pure liquid is constant; according to Raoult's law, every molecule of foreign matter occasions the same constant depression. Every liquid, however, has its own constant coefficient of depres-

¹ Proc. Am. Acad. **21**, 158.

² C. R. **87**, 167; **44**, 1431.

sion, which may be found by determining the depression caused by the presence of one molecule of any substance in 100 molecules of the liquid.

The *vapor tension* of a liquid is not constant within the range of ordinary experimentation, since it is a complex function of the temperature and of the nature of the substance. But Raoult has shown that its depression shows a relation to percentage of foreign molecules which is independent of temperature, provided he expresses the depression, not in absolute measure, but as a fraction of the tension of the pure solvent at the same temperature. Then the molecular depression, *i. e.* the product of the molecular weight of the substance dissolved into the relative depression of a 1 per cent. solution, becomes a definite constant for any substances which that particular liquid may dissolve. It is noticeable that this constant's numerical value always approaches very nearly $\frac{1}{100}$ of the molecular weight of the solvent. The constant is therefore likewise independent of the nature of the solvent; one may generalise for *all* solutions, that the tension of the pure solvent is to the actual depression as is the number of molecules of solvent to the number of molecules of substance dissolved.

Laws as simple as these point to conditions, in solutions, very like those existing in the gaseous state. How great this analogy is has been shown in the well matured papers of J. H. van't Hoff¹ on osmotic pressure. Osmotic pressure is the name given by van't Hoff to the force with which a liquid will enter into a cell containing the solution of some substance in that liquid through walls which are pervious to the solvent alone. Pfeffer² had shown that when such a cell is put into a vessel containing the pure solvent, the latter will enter the cell, increasing the bulk of the solution within, until this tendency is counterbalanced by the difference of level in the two vessels or some other pressure. The pressure required to counterbalance this tendency toward endosmosis is always the same for the same concentration of the solution, and for different concentrations is found to be proportionate to the number of molecules dissolved in the unit volume. Whether this osmotic pressure be due to the motions of the dissolved molecules or to the attraction of some other sort which they exert upon the solvent, it is evident that the effect must depend upon the number of molecules per unit volume only when the molecules of the dissolved body are free to act independently of each other, as do the molecules of a gas. What the real kinetic energy of the molecules in such a solution is, we do not decide by drawing this conclusion. Even if it be as great as in a gas, the great resistance which a solvent opposes to diffusion shows that there is a force which greatly diminishes the external effect of this kinetic energy; it can never, therefore, have occurred to van't Hoff to claim that osmotic pres-

¹ Zeit. phys. Chem. 1, 487.

² Monograph: Osmotische Untersuchungen. Leipzig, 1877.

sure is to be measured externally in the same absolute unit as gaseous pressure. But this opinion seems to have gained a foothold, so that the kinetic treatment of the subject is combated by M. Pupin,¹ on the ground that the kinetic energy of the molecules in a solution ought to burst the containing vessel when it was concentrated to what would correspond, in the gaseous state, to a volume under the pressure of many atmospheres. For this reason he demands that osmotic pressure should be treated as a *static* phenomenon. To the writer, Dr. Pupin appears to confound *molar* and *molecular* kinetics. Because the mass as a whole is in equilibrium and at rest, it does not follow that the molecules must be; in fact, very few physicists would care to call any force *static* in the sense that it was not occasioned by kinetic forces held in equilibrium for the moment.

That the vessel is not exploded by the pressure of the molecules, as Dr. Pupin demands, is due to the same force of solution which prevents their evaporating at the free surface. How great this force can become we may guess from the enormous condensation taking place in the absorption of gases by liquids; that the force is a *kinetic* one is shown by its being a function of temperature, a purely kinetic phenomenon. Bredig² has recently endeavored to show how this force can be made to diminish the external effect of the kinetic energy of the molecules of dissolved substance in such a manner that there is still freedom of action within the mass; and upon this line of reasoning we must depend for a final explanation of the phenomena.

For van't Hoff it was, however, sufficient that an osmotic pressure does exist which is dependent upon the kinetic energy of the molecules. By simple application of the method of Carnot's cycle, he shows that the osmotic pressure must be proportional to the absolute temperature, and that, for solutions of gases, it corresponds precisely to the tension of the gas in the solution. A natural inference from all this is that Boyle's, Gay-Lussac's, Henry's and Avogadro's laws find their counterparts in the laws governing osmotic pressure.

Suppose now solutions of two different substances in the same solvent to possess the same tension for the vapor of the latter; it is necessary that they shall also have the same osmotic pressure. For suppose them separated by a wall which is permeable to the solvent alone, but with their free surfaces in communication through the atmosphere. The vapor tension of both being the same, a little of the solvent might distill from one solution to the other without the performance of any work; but if at the same time their osmotic pressure were different, work *would* be performed by the retransfer of the same quantity of solvent through the membranous wall; this would mean a continuous process in an isolated system,

¹ Dissertation: Der osmotische Druck, etc. Berlin, 1889.

² Zeitschr. für phys. Chem. 4, 444.

attended by gain or loss of energy. As this is impossible, equal vapor tension means equal osmotic pressure, and vice versa. Consequently the same number of molecules always produce the same depression of vapor-tension in a solvent. Exactly the same sort of reasoning would show that solutions having the same freezing point have like osmotic pressures. Both of these laws are identical with those found empirically by Raoult. Thermodynamic reasoning further shows that the molecular depression of vapor tension is indeed one hundredth of the molecular weight of the solvent, while the depression of the freezing point depends more directly upon the nature of the solvent, being a function of its latent heat of liquefaction: $t = 0.02 \frac{T^2}{W}$, where T is the absolute temperature of congelation of the pure solvent, W is the latent heat per kilogram, and t is the molecular depression.

These are the main results of van't Hoff's deductions, as far as molecular weight determinations are concerned. They enable us to employ for this purpose, with perfect confidence, observations upon the phenomena of evaporation, freezing, and osmose.

The direct measurement of osmotic pressure, as was done by Pfeffer, is difficult and not universally feasible. On the other hand, de Vries has shown how to compare such pressures by means of plant cells.¹ It is found that the living protoplasm of such cells, placed in a solution whose solvent only can penetrate the membrane, will yield water to the solution if the latter be concentrated, while it will take it up again if the solution is diluted. The protoplasm will therefore recede from the walls of its cell, or again approach it, and this expansion and contraction can be observed with the microscope. By systematic dilution, a point may be determined for every substance where it is isotonic with another, *i. e.* will neither expand nor contract a protoplasm which had come to rest in the other. Interesting as this method is, and capable of yielding good results in the hands of a skillful microscopist, it is hardly useful in the chemical laboratory where, aside from lack of familiarity with microscopic work, the investigator would be hampered by the exclusion of all substances which will kill plant life.

The freezing-point method has recently been reviewed in this magazine; it therefore only remains for the writer to express his view of its scope. While originally only those few liquids were used as solvents whose freezing points approached that of water, recent investigators have successfully employed substances like paraffine and the more fusible metals as the solvent; there are, therefore, few substances which are not amenable to the

¹ Pringsheim's *Jahrbücher für Wissenschaftl. Botanik* **14**, 4. See also *Zeitsch. f. phys. Chemie* **2**, 414. Donders and Hamburger have shown that the same phenomena can be studied in the behavior of blood-corpuscles; *Archiv für Anatomie und Physiologie, Physiol. Abth.* **1886**, p. 476, also *Hamburger, Maandblad voor Natuurwetenschappen*, **1889**, p. 63.

method. But the following errors should be avoided: the use of thermometers not sufficiently sensitive to admit of observations at high dilutions; contenting oneself with observations within too limited a range of concentration to exclude a chance of overlooking abnormal behavior at some point; allowing too great a change of concentration to occur through the separation of the solvent in the solid state; using solvents which have a chemical effect upon the substance under investigation. Substances dissociate in one liquid which remain in complexed molecules in another. Chemists, in applying Raoult's methods, must remember that all electrolytes behave abnormally in aqueous solutions, and that the presence of hydrates may affect the result.

The method of determining the molecular weight from the vapor tension of the solution is not yet applied so generally; but its scope is even greater, because the range of solvents and of temperatures is so largely increased. Raoult and Planck¹ have shown independently of each other that the formula for the molecular weight of the dissolved substance is

$$M = M_0 \frac{p \cdot f'}{f - f'}$$

where M_0 is the molecular weight of the solvent, p the percentage of substance in 100 grams of solvent, f and f' the tensions of the pure solvent and the solution respectively.

Raoult measures f and f' by the heights of the mercury in eudiometers containing the liquids. A knowledge of the true value of p depends upon the determination of f' , as part of the solvent leaves the solution as vapor under that tension; therefore an error in determining f' affects the result three times in the same direction. The method is less exact and more inconvenient than that of determining the freezing point.

A dynamic way, applied under Ostwald's direction by Walker,² is very much easier: determine the amount of water which different solutions will yield to the same amount of air. The measurements are made on the balance, and the apparatus consists of one set of bulbs to contain the solution, another to hold an absorbent for water, and an aspirator. The method has been generalised by Will and Bredig³ for other solvents.

Lowering the tension means raising the point of ebullition for normal pressure, and the boiling point is, of course, capable of most exact determination. The method has been elaborated by Beckmann,⁴ while the reader will remember a recent paper by Wiley on this subject, which does not, however, give sufficient details, as Beckmann's paper had already been announced.

The latter's apparatus consists of a vessel of about 100 cc. capacity, having a rounded bottom and three necks. Of these,

¹ Zeitschrift phys. Chem. 2, 353 seq., 405 seq.

² Berichte 20, 1084.

³ Zeitschrift phys. Chem. 2, 602.

⁴ Zeitschrift phys. Chem. 4, 532.

the central one connects with a Soxhlet condenser, the second carries a Beckmann thermometer, whose bulb is completely submerged, and the third neck serves for the introduction of the substance.

Steady boiling is assured by filling the vessel to a certain height with beads or garnets, and by sealing platinum wires into the bottom to promote conduction. The pure solvent is first raised to the boiling point, its temperature noted, and the weighed substance is thereupon introduced. As soon as the thermometer has become constant, the rise is noted; a fresh quantity of substance may then be introduced, and the observation repeated. The formula for the molecular elevation of the boiling point is precisely like that found by van't Hoff for the freezing point,

$$t = \frac{0.02 T^2}{W},$$

with the exception that here T means the boiling point of the pure liquid and W its heat of vaporisation. The constant t being found by calculation or experiment, whenever we determine that for p grams of substance to 100 grams of solvent there is an elevation e , the molecular weight of the substance being M ,

$$M = \frac{pt}{e}.$$

The experimental data to show the value of this method have not been published as yet, but it appears to be destined to play as great a part as does the freezing-point method introduced in its most convenient form by the same chemist.

MORRIS LOEB.

LES ORIGINES DE L'ALCHIMIE. Par M. BERTHELOT, Membre de l'Institut. Paris, George Steinheil, Editeur.

As the title indicates, this book is not a complete history of alchemy. The author's purpose is to show how the problem of transmutation of common into precious metals came to be suggested to the minds of men, and where the theories and practices of alchemy came from. The author says (p. 2): "The history of alchemy is very obscure. It is a science apparently without origin, which appears suddenly about the time of the fall of the Roman Empire, and which develops throughout the Middle Ages, amid mysteries and symbols, remaining all the while a secret and persecuted doctrine, under the ban of the Church. Its real scholars are confounded with the deluded, with charlatans, and sometimes with the unprincipled. This history deserves to be taken up, in its whole extent, according to the methods of modern critical investigation. Without undertaking so extensive a research, which would require the whole lifetime of a scholar, I desire to attempt

to penetrate the mystery of the origin of alchemy, and to show by what lines it is connected with the industrial processes of the ancient Egyptians, with the speculative theories of the Greek philosophers, and with the mystic dreams of the Alexandrians and Gnostics."

The work is divided into four books, as follows: 1, the sources, 2, the persons, 3, the facts, 4, the theories.

In the first book is given the historical evidence to show that among the ancient Egyptians, the Chaldeans, the Greeks, and the Jews, there existed the germs of alchemy, partly in the form of facts involved in industrial processes, such as metallurgy, partly in the form of speculative ideas and of mystic and religious theories. It appears that alchemy was first practiced in Egypt as early, probably, as the second century of our era, and that it resulted from the fusion, at Alexandria, of the learning of Greece with that of Egypt and Chaldea. From Egypt came the practical features, mingled with something of the religious or mystic; from Chaldea, more of the latter than of the former; from Greece, portions of philosophy peculiar to the Ionic and Platonic school, pertaining to the constitution of matter. The first alchemists were Gnostics (a name applied to the followers of a system which was a fantastical combination of oriental and Greek philosophy with the doctrines of Christianity). Gnosticism played an important part in all the East, and particularly in Alexandria in the second century of our era.

From the following (pp. 52-3) it is to be inferred that alchemy, once started, spread rapidly over the world: "Alchemy appeared in China in the third century, at the same period in which it flourished in Egypt among the Alexandrians. . . . They find in the great encyclopedia *Pei-ouen-yun-fou*, which in China possesses great authority, this very plain statement: 'The first who refined the *Tan* (transmutation of metals) was one named *K'o-hong*, who lived at the time of the dynasty of *Ou*.' The dynasty of *Ou* reigned from 222 A. D. to 277 A. D. It was, then, about the middle of the third century when the Chinese commenced to practice alchemy."

The remainder of the first book is given to a description of the more important manuscripts referred to for historical evidence. M. Berthelot has not confined himself to consulting the statements found in the histories of Kopp and Hoefer, but he has delved in the great libraries of Europe and has succeeded in bringing forth the most ancient documents known, bearing on the subject of alchemy, the principal contents of which now come to us in this volume for the first time.

In the second book is stated what is known about those alchemists whose names appear in the manuscripts. Some of these personages are purely mythical; some assumed the names of well-known historical personages, and in this way we account for the appearance in the *rôle* of alchemists of such names as Moses,

Queen Cleopatra, Plato, Aristotle, etc. The Greek alchemists, properly so called, are more tangible individuals, such as Zosimus, Africanus, Olympiodorus, etc., considerable portions of whose writings have come down to us.

The third book is devoted to a statement of such practical chemical facts as were known to the Egyptians, such, for example, as concerned the preparation and coloring of the metals and their alloys, and the preparation of artificial precious stones. The very little known in regard to the old Egyptian laboratories is stated in this connection.

The last book contains a statement of such theories of the Greek philosophers as formed the germs of the theories of the alchemists; and, finally, these theories of the alchemists are compared with certain ideas prevailing to-day in regard to the constitution of matter. The ideas of the first alchemists are pretty clearly shown to have been closely connected with the philosophy of Plato, and particularly with the theories expressed in Plato's *Timaeus*.

The author's general conclusions as to the origin and growth of alchemy may be summed up as follows: The first ideas of transmutation of metals came from Egypt and Chaldea, and their origin is lost in antiquity, probably very remote. The Greeks of Egypt transformed these practices into a theory, half scientific, half mystic, just about as they did in case of astrology. From Egypt alchemy was carried to Constantinople in the course of shifting events, and about the seventh or eighth century was transmitted to the Arabs. Finally, the Arabs of Syria and of Spain carried alchemy to Europe.

While M. Berthelot's work has not revealed any startling discoveries, the results of his research have furnished a more satisfactory basis for the historical study of alchemy than we have hitherto possessed. Many connections which were previously only suspected or guessed at may now be regarded as having a fairly good historical basis. M. Berthelot devoted much of his time for six years to this study, the results of which are given in this book. We can understand something of the student-heroism of his undertaking when he tells us that he has read the original passages of all the Greek and Latin references, and, in order to do this, he had to renew his knowledge of Greek by rubbing off the accumulation of forty years' rust.

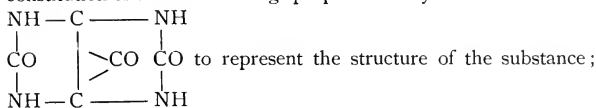
The heavy paper, the generous margins, and the large clear type combine to make a volume which will delight the eye of any one who looks for beauty of this kind in books. An appendix furnishes details of interest in regard to several of the manuscripts cited. Then comes a carefully prepared analytical table of contents, and finally an extremely elaborate index, first of names and then of words.

L. L. VAN SLYKE.

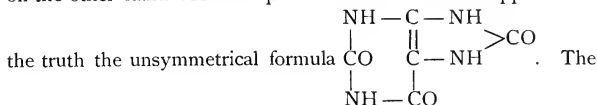
NOTES.

A New Synthesis of Uric Acid.

During the past few years much notable work has been accomplished which had for its end the solution of the problem of the constitution of uric acid. Fittig¹ proposed the symmetrical formula

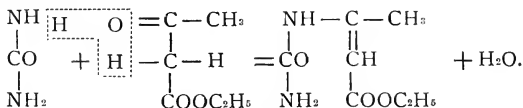


on the other hand Medicus² put forward as a nearer approach to



work of Fischer³ has added much to the evidence in favor of the latter conception ; while the brilliant syntheses of Horbaczewski,⁴ although of the greatest interest, yet on account of the very meagre yield and of the difficulty encountered in attempting to explain the transformations brought about, cannot be said to have hastened much the final solution of the problem. A new method of synthesis has been described by Behrend and Roosen⁵ which seems to show that the formula suggested by Medicus is in all probability correct. The following is a short abstract of the paper of these investigators which describes the synthesis of isobarbituric acid by Behrend⁶ as well as the conversion of the latter into uric acid.

(1) Heated together, ethyl aceto-acetate and urea combine with loss of the elements of water to form the ethyl ether of β -uramidocrotonic acid :



(2) Through saponification by means of caustic potash this ether

¹ Grundriss d. org. Chemie, 10te Aufl. s. 309.

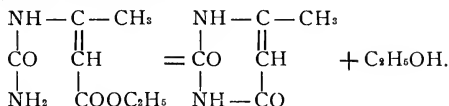
⁴ Monatsh. Chem. 1882, 796; 1885, 356; 1887, 201, 584.

⁶ Ann. Chem. (Liebig) 251, 235. ⁵ Ibid. 229, 39.

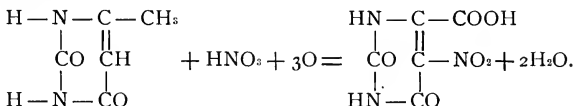
² Ann. Chem. (Liebig) 175, 230.

³ Ber. d. chem. Ges. 17, 1776.

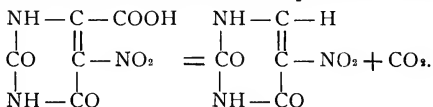
is converted into the potassium salt of β -uramidocrotonic acid, and the acid when in the free condition is decomposed into water and the anhydride, methyluracil:



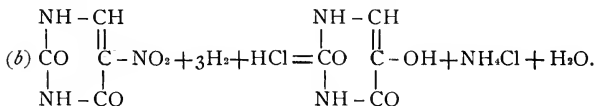
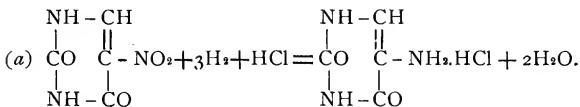
(3) Fuming nitric acid converts this anhydride into nitro-uracil-carbonic acid:



(4) When heated to 130° the potassium salt of this acid breaks down with loss of carbon dioxide to form potassium nitro-uracil:



(5) Upon reduction by means of tin and hydrochloric acid, nitro-uracil is converted partly into amido-uracil, partly into isobarbituric acid.

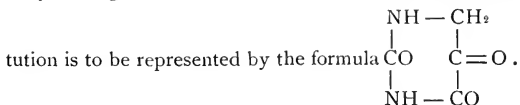


According to Behrend,¹ the condition $\begin{array}{c} \text{NH}-\text{CH} \\ | \quad || \\ \text{CO} \quad \text{C}-\text{OH} \\ | \quad | \\ \text{NH}-\text{CO} \end{array}$ is not a

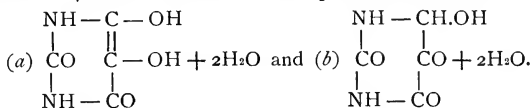
stable one, and the rearrangement which the substance immedi-

¹Ann. Chem. (Liebig) 229, 40.

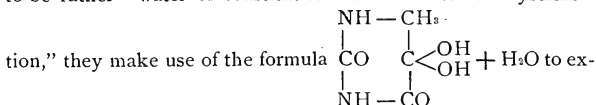
ately undergoes results in the formation of an acid whose consti-



(6) Behrend and Roosen now find that this isobarbituric acid is, upon treatment with bromine water, oxidised to isodialuric acid, $\text{C}_4\text{H}_4\text{N}_2\text{O}_4 + 2\text{H}_2\text{O}$, for which the two possible formulas are:

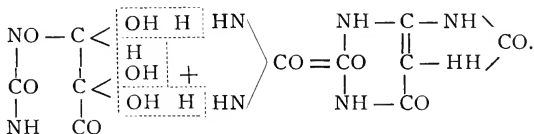


The action of hydroxylamine upon isodialuric acid leads the authors to conclude that the formula (b) is the correct representation of the structure of the compound. Since, however, in the hydrated form of the acid, one of the molecules of water appears to be rather "water of constitution" than "water of crystallisa-



press the constitution of the hydrated acid. Amidouracil, upon oxidation by means of bromine water, yields the same product, isodialuric acid.

(7) Finally, in the presence of sulphuric acid, a mixture of isodialuric acid and urea combine, water being abstracted, with production of uric acid:

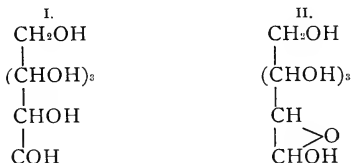


Experiments upon the comparative solubility of the natural and synthetically prepared uric acid in water were made by the authors, and salts of sodium, potassium, calcium, barium, and magnesium were obtained from both varieties of acid. Allantoïn was also prepared from the natural as well as from the synthetically obtained acid. A careful study of the comparative behavior of these derivatives and of the two acids showed that they are identical.

W. W. RANDALL.

Constitution of Dextrose.

Dextrose is usually regarded as an aldehyde alcohol containing five hydroxyl groups. There is, however, another view possible, as first suggested by Fittig, and recently advocated by Tollens, according to which dextrose is the inner anhydride of a heptacid alcohol.



If this anhydride, as represented in formula II, be conceived as taking up water to form the heptacid alcohol, and this then again loses water, the result would be an aldehyde of formula I. This would explain the reactions of dextrose in which it seems to be an aldehyde, and the conduct of dextrose towards phenylhydrazine could not be regarded as a proof of the correctness of formula I.

In order to decide which of these two formulas is the correct one, Z. H. Skraup¹ makes use of a pentabenzoyl derivative of dextrose, which he describes in another article. If formula I be correct, then the pentabenzoyl derivative must be an aldehyde and will show all the characteristic conduct of an aldehyde; that is, it should yield a pentabenzoyl gluconic acid and also a pentabenzoyl dextrose phenylhydrazine compound. If on the other hand formula II be correct, the pentabenzoyl derivative could neither yield a hydrazine derivative nor a carbonic acid. It is hence possible to determine the constitution of the dextrose pentabenzoate and of dextrose itself, by the action of phenylhydrazine and by the action of oxidising agents upon pentabenzoyl dextrose.

Skraup found it impossible to obtain either a normal, phenylhydrazine derivative or a phenylpentabenzoyl glucosazon from the dextrose pentabenzoate by treatment with phenylhydrazine. The reaction with phenylhydrazine therefore affords no proof of the correctness of the aldehyde formula for dextrose.

On oxidation with potassium permanganate, as well as with nitric and chromic acids, no pentabenzoyl gluconic acid was obtained.

These facts make it exceedingly improbable that the pentabenzoyl dextrose is an aldehyde, and lead to the Fittig-Tollens formula for dextrose; nevertheless it cannot be denied that dextrose conducts itself in many of its reactions as an aldehyde, and this necessitates the assumption of a transition of the two forms in one or the other direction.

The peculiar optical property of bi-rotation of dextrose is also in strict accord with this idea of a molecular change.

¹ Monatsh. Chem. 8, 401.

It is well here to remember that the crystallised dextrose $C_6H_{12}O_6 + H_2O$ has exactly the composition of the heptacid alcohol, and it is by no means proved that in this compound the water is present as water of crystallisation. In fact an observation of Soxlet, confirmed by Skraup, that anhydrous dextrose can be crystallised from water in the anhydrous condition, makes the existence of the water of crystallisation in the so-called hydrate of dextrose very doubtful. Skraup endeavors to show that the anhydrous dextrose and the hydrated dextrose differ from each other in their reactions, but without success. When the two substances are treated with phenylhydrazine, he obtains from both an α and a β modification of the dextrose phenylhydrazine. After proving beyond any doubt that these two modifications exist, he states that both result from a replacement of an atom of oxygen, and that this can only be explained on the assumption that the dextrose reacts in different forms with the phenylhydrazine, in the first case as the inner anhydride and in the second as the aldehyde or heptacid alcohol.

Since both the α and the β modification yield the phenyl glucosazon when treated with an aqueous solution of phenylhydrazine acetate, the constitution of the anhydride form of dextrose is fixed. It must be an α anhydride, as shown in formula II.

W. R. ORNDORFF.

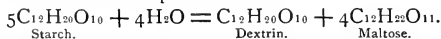
The Molecular Weight of Starch.

Brown and Morris¹ have successfully applied the method of Raoult to the determination of the molecular weights of some of the carbohydrates.

Starch (the variety known as *soluble starch*, prepared by treating ungelatinised potato-starch with hydrochloric acid of 7.5 per cent.) was found to have but a very slight influence upon the freezing point of water, the depression produced corresponding to a molecular weight somewhere between 20,000 and 30,000.

It was at first thought that substances of such a highly colloidal nature as starch might exert only a slight influence on the freezing point of water. Arabinic acid, however, a substance of very marked colloidal properties, exerted a strong influence on the freezing point of water. It seemed probable, therefore, that the small influence observed in the case of soluble starch was really due to the large size of the molecule.

A study of the action of diastase on the starch showed that the act of hydrolysis stops when the amount of dextrin produced corresponds to *one-fifth* the weight of the amount of starch used. The reaction would be expressed thus:



The evidence is almost conclusive that the production of maltose

¹ J. Chem. Soc. (London) 56 (1889), 462.

and dextrin in the above reaction is due to molecular degradation of the starch by hydrolysis. This being the case, it follows that *the molecule of the stable dextrin of the above equation is one-fifth of the size of the soluble starch molecule from which it has been derived.*

The molecular weight of this dextrin was found to correspond approximately to 6480, the figure required by the formula $20(\text{C}_{12}\text{H}_{20}\text{O}_{10})$. The formula of soluble starch would, consequently, be five times this value, or $5(\text{C}_{12}\text{H}_{20}\text{O}_{10})_{20}$. This would give a molecular weight of 32,400, which is in accordance with the approximation (20,000–30,000) obtained by estimating the molecular weight of soluble starch directly.

R. DE ROODE.

Chemical Examination of an Ancient Sceptre.

M. Berthelot has recently discussed the question of the manufacture of bronze by ancient peoples. As copper is widely distributed in nature, the use of that metal might have been expected. Tin, the other constituent of bronze, is on the contrary found in but few localities, and even these are of comparatively difficult access. The positive statements, therefore, which have hitherto been made concerning the general use of bronze by prehistoric peoples have for a long time puzzled those who have given the matter attention. Archæologists agree that the use of unalloyed copper for arms and utensils preceded that of bronze, but the date of the introduction of the alloy of copper and tin has never been satisfactorily settled. Among the many so-called bronze implements contained in collections of Egyptian antiquities, one, the sceptre of Pepi I, a king of the 6th dynasty, archæologists have agreed belongs to an age between 35 and 40 centuries before the Christian era. From the interior of this sceptre some small fragments of the metal were dislodged, and sent by the director of the British Museum to M. Berthelot. An analysis of these particles failed to indicate the presence of even a trace of tin or of zinc. From this M. Berthelot argues that bronze was unknown at this epoch, as otherwise it would have been used in this instance instead of the softer copper. He comes finally to the conclusion, based upon this and other proof, that the art of bronze manufacture has not been known at any rate for more than from fifty to sixty centuries.—(*Ann. Chim. Phys.*)

W. W. RANDALL.

On the Arrangement of the Atoms in Space in Molecules containing Nitrogen.

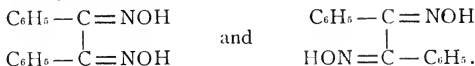
A. Hantzsch and Alfred Werner¹ have proposed an interesting extension of the conceptions of Le Bel, van't Hoff and Wislicenus, with the object of explaining certain cases of isomerism observed among compounds containing nitrogen which cannot be accounted

¹ Ber. d. chem. Gesell. 23, 11 (1890).

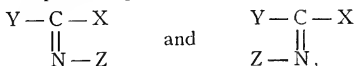
for by the usual conceptions of stereo-chemistry. K. Auwers and V. Meyer have shown that there are two compounds of the structure $\text{C}_6\text{H}_5-\text{C}=\text{C}-\text{C}_6\text{H}_5$. They have suggested that there may



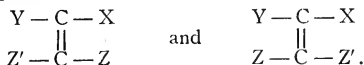
be a kind of single union between carbon atoms which does not permit of free rotation, and that the stereo-chemical formulas of the two compounds may be



Hantzsch and Werner, however, think it more probable that the seat of the isomerism is to be found in the relations of the nitrogen atom to the rest of the molecule. We may conceive of the nitrogen atom being situated at one of the solid angles of a tetrahedron and exerting its affinities in the direction of the three edges of the tetrahedron. Then, whenever a nitrogen atom is united to a carbon atom by two bonds, a possibility of isomerism would exist. Thus, take any compound $\text{YXC}=\text{NZ}$. Two arrangements in space are possible, viz.:



and these bear to each other very much the same relations as the the two compounds:

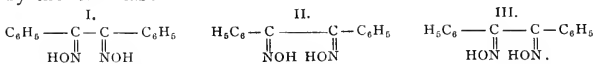


According to this view, three compounds of the formula $\text{C}_6\text{H}_5-\text{C}=\text{C}-\text{C}_6\text{H}_5$



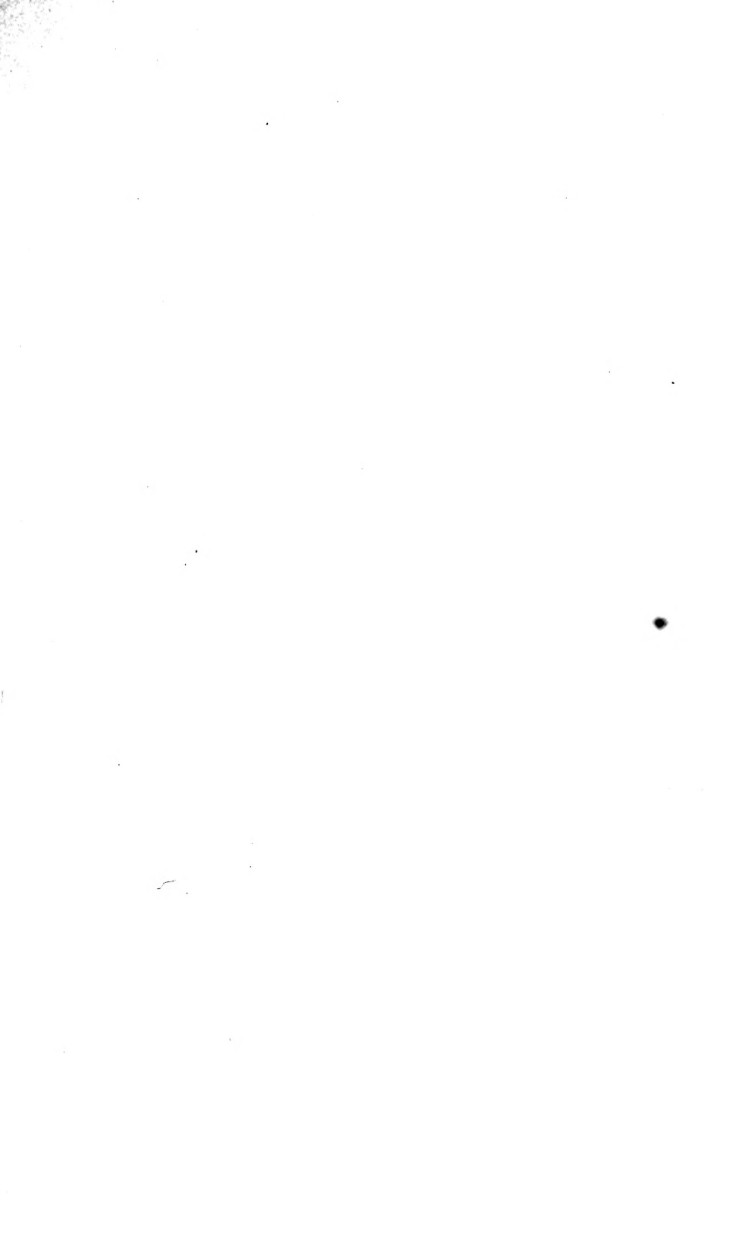
are possible. These are represented

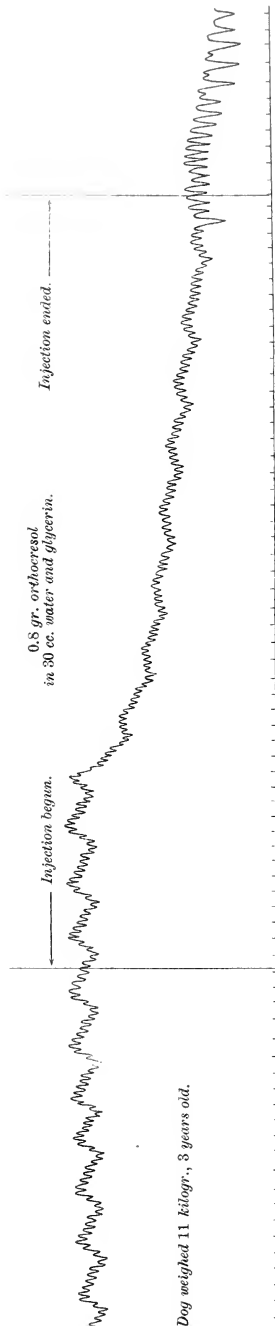
by the formulas:



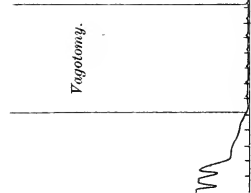
This kind of isomerism is also possible in the case of compounds of the formula $\begin{array}{c} \text{NX} \\ \parallel \\ \text{NY} \end{array}$, and an example of this kind seems to be that of the two trinitroazotoluenes $\text{CH}_3(\text{NO}_2)\text{H}_5\text{C}_6\text{N}=\text{NC}_6\text{H}_2(\text{NO}_2)_2\text{CH}_3$, which, according to Janowski, have the same structure.

I. R.





Dog weighed 11 kilogr., 3 years old.



Death.

AMERICAN CHEMICAL JOURNAL.

A SYSTEMATIC STUDY OF THE ACTION OF DEFIN- ITELY RELATED CHEMICAL COMPOUNDS UPON ANIMALS.

BY WOLCOTT GIBBS, M. D., *Rumford Professor (Emeritus) in Harvard University*, AND H. A. HARE, M. D., *Demonstrator of Therapeutics and Instructor in Physical Diagnosis in the Medical Department and in Physiology in the Biological Department of the University of Pennsylvania.*

II.

(Continued from Vol. XI, p. 448.)

When ortho-cresol is injected into the jugular vein of a dog in the dose of 0.025 gram to the kilo, dissolved in 30 cc. of glycerin and water, almost convulsive struggles come on followed by staggering, the hind legs being most affected. The animal seems stupid and thrills run through the muscles, but the temperature as taken in the rectum only decreases 3 or 4 tenths of a degree Fahr. Later rapid recovery takes place, the animal running about as usual, in as short a time as twenty minutes. We believe these nervous symptoms to be largely dependent on the cardiac depression produced by the injection of the drug. If as much as 0.066 gram to the kilo is used the symptoms become more marked and saliva dribbles from the mouth, the hind legs being again most affected by the paralysis. No change of moment occurs in the rectal temperature, and in forty minutes the dog seems as well as before the

drug was given. Two hours after the dose the animal recovered entirely and chased a monkey around the room, with no failure of motion whatever.

Given to the frog in the dose of 0.004 gram to the gram, hypodermically into the posterior lymph sac, ortho-cresol causes a loss of reflex action in the hind legs particularly; the muscles and nerves rapidly fail to respond to galvanic stimuli before voluntary movement is lost, and death rapidly occurs from cardiac failure, the heart being found widely dilated and paralysed.

When only 0.0003 gram is placed beneath the skin on the back, in five minutes incoördination and loss of reflex activity come on with relaxation, followed by an increase in reflex activity, which in turn gives way to a decrease, which ends in death. As the primary decrease does not occur to any great extent if the center of Setschenow is cut off, the primary decrease in reflex activity is probably due to stimulation of this center.

Reflexes fail *pari passu* with the failure of electricity make nerves and muscles respond.

Applied locally to the heart, it causes a white scar on its surface and stops it in diastole.

This compound in the dog produces a tracing of a very extraordinary character (see tracing 1), causing a rapid fall of blood pressure from 124 mm. of mercury to 18 mm. in one minute and a half from the beginning of the injection, when given in the dose of 0.08 gram to the kilo, accompanied by a slowing of the pulse rate from 156 to 102, and finally causing the pen to run along the abscissa line without marking any pulse wave on the drum.

That the fall of pressure is largely vaso-motor is proved by the character of the fall and the fact that asphyxia produces no rise, although if advanced cardiac weakness were present this would be of no value as a test. As the pulse waves immediately before the stoppage were large, but the rate slow, it occurred to us that the arrest might be due to centric inhibitory stimulation, and this was proved to be partly the case by the fact that upon vagal section the heart beat at 90 per minute, the pulse wave returning for a few seconds. That the stoppage is not entirely due to a centric inhibitory action, however, is evident, since this change was immediately followed by arrest only to be once more replaced by a few beats for 20 seconds at the rate of 60 per 60 seconds, the pressure being from 2 to 26 and then 2 to 14 mm. of mercury;

death coming on ten seconds later. In another animal which was curarised and in which the normal arterial pressure was 144 mm. of mercury with a pulse rate at 120 per minute, the dose of 0.033 gram to every kilo caused a fall of pressure amounting to 27 mm. of mercury, and no noteworthy change of pulse rate until three minutes later, when it became much slower, only amounting to 84 per minute, although the pressure at this time had returned to the normal, save that by its range and peculiar scope it seemed to be caused by a heart beat influenced by vagal stimulation. In order to test this point, section of these nerves was immediately made, with the result that the pulse rate became a little faster, but still remained slow, only reaching 90 per minute. It would seem probable, therefore, that two factors are present in the cardiac action of ortho-cresol, viz. cardiac inhibition and depression. Inhibition, because the pulse waves do not show a heart sufficiently paralysed to cause death, and because vagal section sets the heart going for a moment when it is stopped. Depression, because the heart is found relaxed and paralysed after death, and because section of the vagus will not bring on complete cardiac restoration of function. The cardiac depression is also proved by the results obtained by the application of the drug to the heart of the frog. It is worthy of remark that the blood pressure seems to be directly affected by the drug, as well as secondarily influenced by the alterations in cardiac action due to vagal influences, for asphyxia will not cause a rise in pressure.

Meta-cresol given in the dose of 0.05 gram to the kilo of the dog by the jugular vein, well diluted, produces scarcely any noticeable changes save a slight and very fleeting weakening of the muscles which lasts perhaps three or four minutes. The rectal temperature is unaffected, and in a very short time (thirty minutes) the animal is playful and mischievous, entirely well.

When 0.0022 gram to the gram is given to the frog, hypodermically, lassitude, relaxation and partial abolition of reflex action comes on in the hind legs, the fore legs being less affected. The heart is markedly dicrotic and the circulation is poor, as is evinced by venous congestion of the legs and body. Larger doses, 0.044 gram to the gram, cause rapid loss of reflex action and failure of response of muscle and nerve to galvanic stimuli,

before voluntary motion is lost. The heart is at first markedly dicrotic, the venous system is engorged, and the heart finally is stopped in wide diastole. Separation of Setschenow's center from the body does not cause return of reflexes. The hind legs are most affected.

The primary loss of reflex depends on depression of the sensory centers in the spinal cord and sensory nerves followed by depression of the motor cord and the nerves and muscles, as has been proved by finding all these parts lacking in response to galvanic stimuli.

That the paralyzing action is profound is proved by the fact that even $\frac{1}{2}$ of a grain of strychnine given hypodermically fails to cause any sign of a convulsion.

Meta-cresol when given by the jugular vein in the dose of 0.09 gram to the kilo, dissolved in 30 cc. of water and glycerin, causes a slight slowing of pulse rate accompanied by a very marked fall of blood pressure, so that while the pulse rate drops from 180 to 150 beats (30 beats), the pressure falls from 140 mm. of mercury to 42 mm. of mercury, and then after the lapse of two minutes reaches 75 mm., the pulse rate has also by this time returned to the rate existing before the drug was given (180). It is to be noted that even when the pressure is lowest the pulse waves are well developed and more full than is common in great cardiac depression. If, while the pressure is at 75 asphyxia be produced, there is no increase of pressure of any extent, and consequently it is fair to assume that the fall of pressure which takes place is due to vaso-motor depression. Six minutes later, the pressure having risen to 122, a second dose of 0.07 gram to the kilo was given, and immediately a second fall of pressure took place with very slight variation in pulse rate. Four minutes after this, the blood pressure having risen once more 105 mm., one gram was given and produced death in thirty seconds by cardiac failure. That the cardiac arrest was not due to inhibitory stimulation is proved by the fact that section of the vagus nerves, immediately, failed to set the heart in action. In another experiment where the dose was 0.15 to the kilogram, death occurred within twenty seconds from the administration of the dose by the jugular vein, there being a fall of pressure almost to the abscissa line, and a gradual failure of cardiac force as shown by the pulse waves. We therefore conclude that meta-cresol acts as a direct depressant poison to the vaso-motor

system, and also to the heart muscle to a less extent, when given in the dose of from 0.05 gram to 0.20 gram to the kilo of the dog's weight, and that it paralyses all vital tissues with which it comes strongly in contact, affecting the sensory nervous system primarily, and the motor system secondarily, paralysing them.

When para-cresol is injected into the jugular vein of a dog not attached to a manometer, but free to run about, and to which no ether has been given in opening the vein, in the dose of 0.1 gram to the kilo in 40 cc. of water and glycerin, marked struggles of a convulsive character come on, amounting finally to a tonic spasm of a moment's duration. Following this is some staggering of gait and evidences of weakness, particularly in the hind legs, lasting for three minutes. As the animal now rapidly recovers, we believe the spasms and subsequent weakness to be due to the circulatory disturbance produced by the drug thrown into the heart *en masse*. There is absolutely no change in the rectal temperature as a result of the use of the drug, and in an hour or so the animal seems as well as ever.

When 0.006 gram to the gram is injected into the posterior lymph sac of a frog, death comes on almost at once, the heart being stopped in diastole. There is response to stimuli in the limbs, which are stiffened almost as with *rigor mortis*.

If 0.002 gram to the gram is given, a few jumps take place as the result of the irritation, reflex action is lost, and incoordination ensues. Crawling takes the place of jumping. Section of the spinal cord to cut off any influences from Setschenow's center fails to restore reflex activity, but later reflexes return and become excessive. The muscles and nerves respond to galvanic stimulus sluggishly. The hind legs seem most affected. The same results, but of a severe character, come on when 0.02 gram is given, the hind legs being merely dragged after the body which is moved by the fore feet, the latter seeming with the nose hyper-sensitive. The muscles and nerves in the hind legs respond poorly to electricity. There is always very marked loss of sensation, due to an action on the receptive side of the spinal cord and also on the sensory nerves. Locally applied to the exposed beating heart it acts as a depressant poison, stopping it very shortly in diastole. From these tests on the dog and frog it would seem proved that

para-cresol acts as a depressant poison to all tissues with which it comes in contact, if in concentrated form, and that while its dominant action is on the circulatory system, it paralyses first the sensory nervous system and then the motor, the posterior parts of the body being most affected.

Para-cresol, when given to a dog by the jugular vein in the dose of 0.08 gram to the kilo, produces immediately a very marked and sudden fall in the blood pressure, with a corresponding decrease in pulse rate. The fall of pressure may amount to nearly 100 mm. of mercury, in from thirty seconds to a minute, and is so sudden as to be very evidently dependent upon cardiac depression and not vaso-motor influence. Immediately after this the pressure rises nearly to the normal as the heart rids itself of the poison. If a second dose be now given a greater fall takes place than before, the pressure equalling only 4 mm. while the pulse also becomes still slower. After the lapse of three minutes from the last dose the pressure partially recovers itself, but the pulse rate remains very much slower than the normal. The pulse waves are also fairly full and stronger than they were immediately after the drug was injected. In order to determine whether the slow rate was inhibitory in its nature the vagus nerves were severed, but the rate and pressure did not increase as they do in the non-poisoned animal under such circumstances. Ten minutes later another dose of 0.04 gram to the kilo produced a fall of pressure and rate followed by a partially compensatory rise of pressure, which, however, immediately fell in death when 0.16 gram to the kilo of the animal's weight was injected in two equally divided doses, twenty seconds apart. The question at once arises as to whether the fall of pulse rate and pressure was entirely due in every instance to cardiac depression, or whether the inhibitory nerves were also stimulated peripherally. This is almost impossible to answer. The cardiac depression was certainly present, and the pneumogastric stimulation peripherally was probably a factor, since other experiments in which smaller doses were used caused cardiac slowing without much cardiac depression: 0.1 gram to the kilo stops the heart in diastolic arrest.

CONCLUSIONS.

Ortho-cresol on the heart of the dog and frog acts as a depressant poison. It causes in the frog paralysis of the spinal cord and

sensory and motor nerves, the sensory apparatus being most affected, and diminishes the contractibility of the muscles. It would seem to be a stimulant at first to Setschenow's reflex inhibitory center.

Ortho-cresol produces death by cardiac arrest by depressing this viscus and by stimulating somewhat the centric inhibitory apparatus, when given in the dose of 0.08 gram to the kilo. The depression of the vaso-motor apparatus is also an important factor in producing the fatal issue.

When given in the dose of 0.033 gram to the kilo it slows the pulse by depressing the heart and stimulating the vagus nerves.

Ortho-cresol is, therefore, in small amounts a stimulant to inhibitory nervous protoplasm, and in larger amounts a powerful depressant to all vital tissues.

Meta-cresol has no influence on the inhibitory apparatus of the frog or dog as have ortho- and para-cresol. It is not so powerful a cardiac depressant, but acts more upon the vaso-motor system. On the nervous system it paralyses the sensory and finally the motor apparatus of the body. In the dose of 0.07 to 0.09 gram to the kilo of the dog's weight by the jugular vein it causes cardiac depression, but chiefly acts on the vaso-motor apparatus. When given in as large a dose as 0.15 gram to the kilo by the jugular it produces death by cardiac arrest.

Para-cresol acts upon the frog and dog as a depressant poison to the heart, and secondarily to the nervous system, particularly the sensory apparatus; afterward the nerves and muscles and motor tract of cord are paralysed. In the dog, para-cresol, in the dose of 0.1 gram to the kilo, causes death by cardiac paralysis. In the dose of 0.08 gram to the kilo the pulse becomes slow from a stimulation of the inhibitory apparatus centrically, and perhaps peripherally, accompanied by depression of the cardiac muscle, the vaso-motor system seeming but little if at all affected.

Résumé.

Ortho-, meta- and para-cresol all act as sensory and motor paralyzants.

The ortho and para compounds act as stimulants to inhibitory processes; the meta compound has no such influence. The ortho compound seems to be the more powerful inhibitory stimulant of the two, and is the most powerful cardiac depressant of the group.

After ortho-cresol in this respect is para-cresol; meta-cresol having little cardiac influence comparatively; thus, ortho-cresol kills when injected in the strength of 0.08 gram to the kilo, para-cresol in the dose of 0.1 gram to the kilo, and meta-cresol when the amount equals 0.15 gram to the kilo.

Meta-cresol seems to affect the vaso-motor system more than para-cresol, but probably not more than ortho-cresol.

Ortho-cresol and para-cresol are grouped as inhibitory stimulants and cardiac depressants; ortho-cresol and meta-cresol as vaso-motor depressants. On the nervous system of the frog these compounds act as paralysants in the same order as they act upon the heart. Thus of ortho-cresol 0.004 to the kilogram paralyses nerves and causes death. Para-cresol kills at 0.006; meta-cresol only at 0.044 gram to the kilogram.

THE HYDRO-ELECTRIC EFFECT OF STRETCHING METALS.

By C. BARUS.

1. The question which forms the subject of the present paper has an important bearing on many problems connected with the viscosity of solids. It is for this reason that I undertook the work.

2. The hydro-electric method is usually conceded to be the most delicate for testing differences of molecular constitution in metals. Hence if a change of molecular structure be among the results of a mechanical strain of any kind imparted to a metal, the change of its electro-positive quality will probably indicate the molecular change. Unfortunately, hydro-electric data are always distorted by polarisation. Polarisation, moreover, is apt to be even larger than the effect to be studied, so that the observer is obliged to resort to methods of measurement in which a fair degree of constancy of the error in question is assured. It follows that unless the hydro-electric effects are as large, for instance, as those produced by temper in steel,¹ the effect of strains which cannot be applied without removing the wire or metal from the hydro-electric

¹ Barus and Strouhal, *Am. Jour. Sci.* 32, 276, 1886.

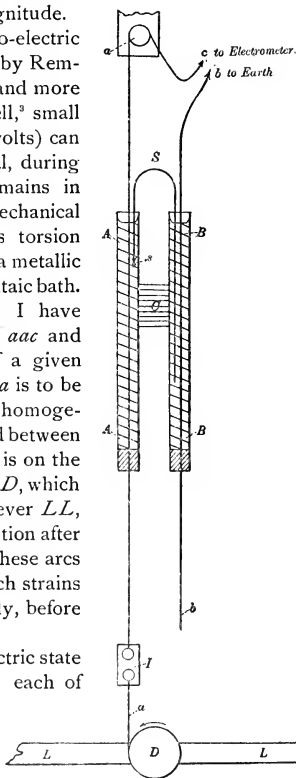
bath is not observable. In such a case the polarisation varies with each immersion in a way quite beyond control. Moreover, certain strains like the drawn strain show different mechanical conditions at different distances from the axis. Hence the hydro-electric constant of such a rod, were it obtainable, would be a complex magnitude.

In magnetisation, the hydro-electric effect of which was discovered by Remsen¹ and studied by Nichols,² and more recently by Rowland and Bell,³ small hydro-electric effects ($< .03$ volts) can be detected because the metal, during straining (magnetisation), remains in place. Among ordinary mechanical strains, traction and perhaps torsion admit of similar application to a metallic wire, left undisturbed in the voltaic bath.

3. In the annexed figure I have shown the apparatus used. *aac* and *bb* are consecutive pieces of a given kind of soft wire. Of these *aa* is to be stretched, *bb* examined in the homogeneous state. Hence *aa* is fixed between two points of which the lower is on the circumference of an iron drum *D*, which can be rotated by aid of the lever *LL*, and is frictionally fixed in position after any arc of rotation. Usually these arcs were 180° , and four or five such strains could be applied consecutively, before rupture ensued.

Measurements of hydro-electric state were made before and after each of these strains. For this purpose both wires were surrounded by a glass tube *AA* and *BB*, respectively,

held together by a little block of wood *C*. These tubes were closed



¹ Remsen, this Journal 3, 157, 1881.

² Nichols, Am. Jour. Sci. 31, 272, 1886; Ibid. 35, 290, 1888.

³ Rowland and Bell, Phil. Mag. (5) 26, 105, 1888.

below with rubber corks, through which the wires passed without leakage. The tubes were filled either with a concentrated solution of zinc sulphate, with distilled water, or with any other liquid which does not act strongly on the metal. The electrolytic connection between *AA* and *BB* was made by a siphon *S*, filled with the liquid of the tubes and closed at *s* with a parchment septum. The upper ends of the wires *b* and *c* were in connection with the terminals of a Mascart electrometer, or with the wires of an apparatus for zero method.

After straining the wire *aac* to the point of breakage, the apparatus was reversed and *bb* now strained in the same manner, *aac* being free. In this way the number of distinct measurements for each adjustment was doubled.

The wire being 54 cm. long and the diameter of the drum about 1.7 cm., the extension of the wire per rotation of 180° was about 2.6 cm., or $\delta L/L = .05$, nearly. The amount differed slightly when wires of different thicknesses were used. The reduction of the diameter of iron wire before and after straining is therefore considerable.

4. The hydro-electric effect of traction is characterised by a temporary and a relatively permanent part. The temporary part may be studied by observing the throw of the needle immediately after straining, as well as the differences of the potential at the end of each of the following minutes. The difference of potential which remains after the temporary effect has subsided I called the permanent part. An allowance of five minutes was usually regarded sufficient. This assumption is somewhat arbitrary; but the errors committed are of like effect throughout the series. The value of the throw is expressed in volts (as are the other electrical data), and is given as an *increment*, that is, without reference to the actual potential of the stretched wire. It is to be noticed, moreover, that the temporary effects are measured *without* commutation. The permanent effects are measured with commutation, each wire being alternately put to earth, while the other is connected with the electrometer (Mascart's key). I made about seven series of the following kind, two of which are given in Table I. The diameter of the wire before straining was $2\rho_1 = .086$ cm.; after straining $2\rho_2 = .078$ cm.

TABLE I.—Hydro-electric Effect of Stretching Iron Wire.

Strain.	Throw $e \times 10^3$ temporary.	$e \times 10^3$ permanent.	Strain.	Throw $e \times 10^3$ temporary.	$e \times 10^3$ permanent.
O	...	+ 9	O	...	+ 0
I	—34	+ 7	I	—18	+ 5
II	— 0	+11	II	— 2	+ 9
III	+ 8	+14	III	+ 5	+11
IV	IV	+10	+13
O	...	—14	O	...	— 6
I	—26	—13	I	—15	— 1
II	— 0	— 8	II	— 0	— 0
III	+10	— 4	III	+ 2	+ 2
IV	+12	— 1	IV	+ 5	+ 3

Extension, $\delta L/L = .05$ per pull. Radial contraction, $\delta \rho/\rho = .022$ per pull. Mean permanent potential increase = +.003 volts per pull.

The table shows that the permanent effect is distinctly electro-positive; negative differences are numerically decreased, positive differences are increased. The increase of electro-positive quality takes place simultaneously with the increase of length, at a rate which varies somewhat in different experiments, but the mean value of which is about .003 volts per extension $\delta L/L = .05$. This is equivalent to a decrease of the wetted external surface of the wire, of about 5 per cent., supposing there is no change in the specific volume of the metal. The measured value is less than this, for the circumference before straining was found to be $2\pi\rho_s = .27$ cm., after straining (aggregate of the four pulls) $2\pi\rho_h = .24$ cm. This is less than 3 per cent. of the wetted surface, per pull.

The temporary effect is equally definite in character. Apart from the value of the permanent effect, the former is at first negative, which (negative) quality is then successively reduced, until by passing through zero it becomes positive. The intensity of the first negative throw is, as a rule, stronger than the final positive throw.

5. It is expedient to indicate in passing some probable cause for the phenomena. Iron submerged in an aqueous solution is polarised positively and covered with a coating of hydrogen. Hence it is practically a condenser, whose capacity increases directly with the wetted surface, *caet. par.* The effect of strain is therefore twofold in kind. If in consequence of the jarring or vibration which unavoidably accompanies stretching, some of the gas is mechanically skaken off, the positive polarisation is decreased.

This is probably indicated by the negative throw of the needle, immediately after the first strain. Simultaneously with this result the capacity of the wire is diminished, in consequence of stretching (wetted surface decreased). Hence the positive polarisation or potential is again increased. If the last effect gradually predominates over the other (effect of jar), the temporary throw changes from negative to positive. This explanation is the nearest at hand and it need not be sufficient; but it is clear at once, that before any hydro-electric change can be ascribed to strain as such, it is necessary to evaluate the polarisation error, as well as other minor errors, such for instance as are due to the increase of the temperature of the wire due to stretching. Cf. Wiedemann's "Elektricität," Vol. II, p. 773, etc.

6. In the following tables I have inserted data corresponding to Table I, but obtained in the same way with German silver, brass, copper and iron, all the wires being of larger diameter than above. The notation is that already used. In Tables II to V a concentrated solution of zinc sulphate is the electrolyte; in the other cases distilled water is used. At the ends of the tables the mean value per pull of the extension, $\delta L/L$, the radial contraction, $\delta\rho/\rho$, and the permanent increase of potential, e volts, are inserted for each wire.

TABLE II.

German silver $\begin{cases} 2\rho_s = .102 \text{ cm.} \\ 2\rho_h = .093 \text{ cm.} \end{cases}$
Zinc sulphate.

Strain.	$\times 10^3$ temporary.					$e \times 10^3$ permanent.
	Throw.	1m.	2m.	3m.	4m.	
O	+27
I	+36	12	12	13	16	+28
II	+42	16	6	— 4	—19	+35
III	+50	19	— 1	—10	—18	+47
IV	+69	42	18	9	2	+51
O	+24
I	+32	13	7	4	4	+30
II	+26
III	+24
IV	+23
V	+18

Extension per pull, $\delta L/L = .05$.

Radial contraction per pull, $\delta\rho/\rho = .022$.

Mean permanent potential increase per pull = .005.

TABLE III.

Brass $\begin{cases} 2\rho_s = .166 \text{ cm} \\ 2\rho_h = .157 \text{ cm.} \end{cases}$

Strain.	$e \times 10^3$ temporary.					$e \times 10^3$ permanent.
	Throw.	1m.	2m.	3m.	4m.	
0	+23
I	+21	18	12	12	13	+39
II	+41	31	28	25	24	+59
III	+48	30	20	18	15	+65
IV
0	-15
I	+17	4	2	0	-2	-18
II	+18	10	6	3	1	-18

Extension, $\delta L/L = .05$ per pull.

Radial contraction, $\delta\rho/\rho = .013$ per pull.

Mean permanent potential increase per pull = .015.

TABLE IV.

Copper, $2\rho_s = .166 \text{ cm.}$

Zinc sulphate, $2\rho_h = .150 \text{ cm.}$

Strain.	$e \times 10^3$ temporary.					$e \times 10^3$ permanent.
	Throw.	1m.	2m.	3m.	4m.	
0	+4
I	0	0	0	0	0	+6
II	0	0	0	0	0	+6
III	+3	2	1	2	2	+6
IV	2	2
0	-6
I } II }	+2	2	2	2	2	± 0
III } IV }	+2	2	2	-1

Extension per pull, .05.

Radial contraction per pull, .024.

Mean permanent potential increase per pull, .001.

TABLE V.

Iron, $2\rho_s = .156$ cm.Zinc sulphate, $2\rho_h = .147$ cm.

Strain.	$\epsilon \times 10^3$ temporary.					$\epsilon \times 10^3$, permanent.
	Throw.	1m.	2m.	3m.	4m.	
O	+8
I	-58	-42	-29	-22	-17	-6
II	-36	-24	-12	-1	-5	-5
III	-22	-3	-2	-2	-1	-3
IV	-36	-24	-17	-14	-10	-7
O	+4
I	-52	-38	-24	-18	-15	-7
II	-30	-17	-10	-6	-4	-7
III	-30	-18	-6	-4	-0	-7

Extension per pull, .05.

Radial contraction per pull, .014.

Mean permanent potential increase per pull, -.003.

TABLE VI.

Brass, $2\rho_s = .166$ cm.Water, $2\rho_h = .154$ cm.

Strain.	$\epsilon \times 10^3$ temporary.					$\epsilon \times 10^3$, permanent.
	Throw.	1m.	2m.	3m.	4m.	
O	-76
I	+82	73	59	48	39	-44
II	+58	40	22	8	-2	-52
III	+63	49	28	14	7	-56
IV	+62	44	27	14	8	-60
O	+73
I	+42	42	42	38	36	+103
II	+21	14	13	8	6	+91
III	+28	21	11	-1	0	+77
IV	+29	24	14	7	3	+67

Extension per pull, .05.

Radial contraction per pull, .018.

Mean permanent potential increase per pull, $\pm .015$

TABLE VII.

Iron, $2\rho_s = .135$ cm.

Water, $2\rho_h = .126$ cm.

Strain.	$e \times 10^3$ temporary.					$e \times 10^3$ permanent
	Throw.	1m.	2m.	3m.	4m.	
O	+16
I	-17	+46	60	67	70	+79
II	-10	+24	28	29	...	+95
O	-56
I	-33	-17	-6	-3	-1	-40
II	-4	+7	+14	-23
III	-6	+13	+14	-6

Extension per pull, .05.

Radial contraction per pull, —

Mean permanent potential increase per pull, +.027.

TABLE VIII.—*Promiscuous Work.*

Copper wire. Distilled water.

Strain.	$e \times 10^3$ temporary.					$e \times 10^3$ permanent.
	Throw.	1m.	2m.	3m.	4m.	
O	+15
Jerk	-42	+2	+4
Jerk	-35	-4	+2
I, II	+29	+28	+29	+34	...	+27
III, IV	+13	+9	+7	+8	...	+28

Extension per pull, .05.

Radial contraction per pull, .024.

Potential increase per pull, .015.

Iron wire. Distilled water.

O	-40
Jerk	-42	-15	-6	+2	...	-39
Jerk	-49	-28	-6	+1	...	-36
Jerk	-45	-21	-7	-36
After long waiting						-18

		Brass wire.		Distilled water.		
O	— 8
Jerk	—21	—25
Jerk	—35	—29
Jerk	—17	—21
Rub	—10
Rub	} no temporary effect	}	}	}	}	— 6
Rub						— 9
O	— 6
I	+35	35	35	31	31	+25

German silver $2\rho = .08$ cm.; zinc sulphate.

Strain.	$e \times 10^3$ permanent.	Strain.	$e \times 10^3$ permanent.
O	+13	O	—1
I	+ 7	I	—6
II	+ 0	II	—6
III	— 6	III	—6

7. Turning first to the permanent hydro-electric effect of traction, Tables II and III show increments of decidedly larger positive value than hold for iron in Table I. The effect for copper in Table IV is nearly zero, and for iron in Table V actually negative. Whatever the effect may be, it must necessarily be considered doubly specific, depending both on the metal and the liquid. Hence I made further investigations in Tables VI, VII and VIII by replacing the zinc sulphate solution by water. Thus it is found that the permanent effect is decidedly greater in magnitude for water than for zinc sulphate, from which the close relation of these phenomena and polarisation may be inferred. The effect in the case of water, moreover, is by no means as regular as in the other case. In Table VI, for instance, the permanent points enclose a figure of rhomboidal outline, showing that the effects of initial pulls are different from the final pulls. Again, copper which in zinc sulphate is not changed hydro-electrically by traction, in water shows effects quite comparable to the other metals. Iron-water data are excessively large. Irrespective of sign, the hydro-electric effect increased with the diameter of wire used.

Among results bearing on section 9 below, I may mention that the permanent effect of traction of iron in zinc sulphate is sometimes positive, sometimes negative, depending on the qualities of

the wire. Table VIII shows a specimen of German silver in which the permanent effect is negative.

I have given the temporary effects in their absolute value (increments) aside from the diameter of the wire. In case of German silver, of brass, of copper, these effects are distinctly positive (opposite in sign to the first iron effects).

Returning to the explanation suggested in section 5, it appears that in German silver, copper and brass the effect of diminished capacity and of exposure of fresh surface¹ due to stretching, both of which are positive, predominate over the negative effect of incidental jerking. In iron, since the temporary effect is first negative, they do not so predominate. It is specially to be noticed that the permanent effect is entirely independent of the temporary effect. Inasmuch as the permanent effect is obtained by commutation (each electrode being alternately put to earth), the residuum of the temporary effect is discharged. From this it might be conjectured that the apparatus acts like a doubled condenser.

In Table VIII, I give some data bearing on the probability of this explanation. The wires were adjusted in the usual way; but instead of being stretched, were only jerked by the action of the machine. In this case a negative temporary effect is obtained in *all* the metals, about of the same numerical order as the data in the earlier tables. Similar results follow after rubbing the immersed parts of the wires.

It might be inferred that the temporary effect is due to friction at the axle of the drum. But I found in special experiments that all such charge escapes to the earth without influencing the electrometer.

8. Since the immersed part of the wire is of the form of a cylinder of length l and radius r , its capacity is approximately

$$C = l/2 \ln \frac{l}{r}.$$

If the charges are constant, so that $Q = VC = V'C'$, or $V/V' = \log r/\log r'$, it follows that (V' and V being identical)

$$V'_1 = \frac{\log r'}{\log r - \log r'} (V - V'). \quad (1)$$

¹ This being at once acted on by the liquid, falls under the considerations made in the text above.

From this expression the polarisation of the wire may be calculated, when the difference of potential due to traction is known. The data of Tables I to VIII then furnish the following values of V'_1 . The subscripts attached to the symbols of the metals refer to the number of the table from which the data are taken.

Metal.	Fe ₁	G. S. ₂	Brass ₃	Cu ₄	Fe ₅	Br ₆	Fe ₇	Cu ₈
$\log r/\log r/r'$	26	26	33	19	32	25	30	19
$\Delta V \times 10^3$	4×3	4×5	4×15	4×1	-4×3	±4×15	4×27	4×15
V'_1	+·31	+·52	+1·98	+·08	—·38	±1·50	+3·24	+1·14
	ZnSO ₄					H ₂ O		

If the wire and its surrounding liquid be regarded a condenser, of which the film of gas (hydrogen) is the medium through which induction takes place, the capacity is

$$C = \frac{r_1 k}{e} \left(1 + \frac{e}{2r_1} \right), \text{ nearly,}$$

where e is the thickness of the film of gas, r_1 the radius of the wire, the specific inductive capacity being $k = 1$. If then the charge be regarded constant as before, an equation similar to (1) may be obtained by introducing some reasonable postulate relative to the thickness e . Suppose e is constant, i. e. before and after pulling the layer of gas is not changed in thickness. Then the potential V'_2 of the immersed wire is

$$V'_2 = \frac{r}{r' - r} (V - V'). \quad (2)$$

Again, suppose the mass of the film of gas to be constant, so that $2\pi r e = 2\pi r' e'$. Then the potential of the immersed wire is

$$V'_3 = \frac{r^2}{r'^2 - r^2} (V - V') \quad (3)$$

On this assumption Tables I to VIII furnish the following digest:

Metal.	Fe ₁	G. S. ₂	Brass ₃	Cu ₄	Fe ₅	Brass ₆	Fe ₇	Cu ₈
V'_2	.12	.21	1.06	.04	—·20	± .76	1.54	.57
V'_3	.22	.38	2.04	.07	—·38	±1.50	3.00	1.08

In discriminating¹ between the values V_1 , V_2 , V_3 , it is clear that

¹ The close analogy of a polarised voltmeter and a double condenser was pointed out by Varley (Phil. Trans. 161, 129, 1872), and investigated by Colley (Wied. Ann. 7, 206, 1879) and others. The subject is minutely discussed in Wiedemann's Elektrizität 2, 758-771. It may be observed that in equation (2) the increment of potential varies as the decrement of wetted surface.

the conditions of V_1 are not given, and that the maximum probability rests with V_2 ; but this quantity is not decidedly above the order of possible polarisation for the cases under discussion. Hence the permanent hydro-electric effect due to a change in the electro-positive quality of a metal by traction is obscured beyond recognition by the unavoidable variations of polarisation which accompany the experiment.

Having thus failed to obtain reliable evidence from hydro-electric experiments, I endeavored with some pains to discern a direct electrical effect (potential) due to the traction of a single insulated wire immersed in an electrolyte. These experiments may be omitted here; they contribute no essentially new data. So far as my work went, no certain permanent indication of a hydro-electric effect of strain could be obtained by any of the methods applied.

9. In the above paragraphs I have endeavored to refer the very definite hydro-electric results obtained to the simplest explanation at hand. But it is necessary to bear in mind that the phenomena are so largely beyond the observer's control that an exhaustive experimental discussion is out of the question. It would be unwise, therefore, to lose sight of other points of view from which they may have a direct bearing on the real question in hand, viz. the possibility of molecular change in a metal, corresponding to each change of strain imparted to it. The question is steadily gaining in probability. Osmond, after making an elaborate pyrometric study of the conditions under which Gore's phenomenon occurs in iron, postulates the existence of an α and a β variety of iron. These varieties when cold may be distinguished physically by their difference in hardness. Moreover, β -iron, besides being produced spontaneously out of α -iron, above a certain temperature in red heat, may also be produced in small quantity by straining α -iron at ordinary temperatures. I pointed out that such an hypothesis involves the occurrence of α and β varieties of most metals, even when no such criterion as is given by Gore's phenomenon is observable. Quite recently Mr. Carus-Wilson,¹ from experiments made on the viscosity of strained steel, summarises his experience in favor of Osmond's²

¹ Carus-Wilson, *Nature* 41, 213, 1890.

² Osmond, *Annales des Mines*, July-August, 1888; *Mém. de l'artillerie de la Marine*, Paris, 1888, p. 4.

view. Unfortunately, the well known effects of strain on the thermo-electric quality and on the resistance of metals are not at once interpretable, except perhaps in so far as they are accompanied by hysteresis (Cohn, Warburg, Ewing, Schumann). The ion theories of metallic electrical conduction now coming into vogue (J. J. Thomson, Giese¹), conditioned as they must be by the occurrence of marked molecular instability in metals, are steps in the same direction. I will therefore merely point out, in concluding, that the simple explanations given above for the temporary effect, which was found consistently negative at first in iron, and consistently positive in all the other metals, is not satisfactory. It is permissible to regard it as the direct result of a change of molecule due to straining; for it is precisely in the first stages of the temporary effect that evidence for such molecular change may reasonably be sought.²

Contributions from the Chemical Laboratory of Harvard College.

LXVII.—ON THE ACTION OF SODIUM ACETACETIC ESTER UPON TRIBROMDINITROBENZOL.

BY C. LORING JACKSON AND GEORGE DUNNING MOORE.³

After the action of sodium malonic ester on tribromtrinitrobenzol and on tribromdinitrobenzol had been studied, it seemed of interest to determine whether sodium acetacetic ester acted in the same way, and the following paper contains the results of experiments undertaken with this intention upon the tribromdinitrobenzol, which was selected because it can be prepared so much more easily than the corresponding trinitro compound. These results can be sum-

¹ Giese, Wied. Ann. **37**, 576, 1889.

² Cf. Rowland and Bell (*l. c.*), who are obliged to base their inferences on the temporary hydro-electric effect of magnetisation. In all problems of this character it is necessary to distinguish between the positional stability and the chemical stability of a molecule. It does not follow that if the former quality is increased, the latter will also be, for a chemical solvent does not pick up molecules bodily, but by disintegrating them. In certain experiments on the isothermal electromotive force of a Daniell between 10 and 1800 atmospheres, I will indicate this further.

³ Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

marised briefly as follows. Tribromdinitrobenzol behaves with sodium acetacetic ester in the same way that it does with sodium malonic ester: that is, one atom of its bromine is replaced by the acetacetic radical



and a second by hydrogen, while the third remains unaltered; so that the product of the action is the bromdinitrophenylacetacetic ester,

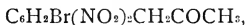


or to speak more accurately its sodium salt,



The bromdinitrophenylacetacetic ester melts at 96° , and possesses marked acid properties, forming the sodium salt whose formula has just been given, even with acid sodic carbonate in aqueous solution. The salt has a red color and is soluble in water; in fact, it resembles the sodium salt of the corresponding malonic compound most closely.

The bromdinitrophenylacetacetic ester is saponified and decomposed by heating with sulphuric acid of specific gravity 1.44, giving the bromdinitrobenzylmethylketone,



but no trace of the corresponding acetic acid. This ketone melts at 112° – 113° , and also possesses acid properties, giving a purplish red salt soluble in alcohol, but decomposed almost completely by water. The acid properties of the ketone are less marked than those of the acetacetic ester, as was to be expected, since the hydrogen, which is replaced by basic radicals, is subject to the influence of an acetyl, a carboxylester and a dinitro phenyl group in the acetacetic compound, only to those of an acetyl and a dinitro phenyl group in the ketone.

The bromine of the ketone can be replaced easily by the aniline radical $\text{C}_6\text{H}_5\text{NH}$, forming anilidodinitrobenzylmethylketone,



which melts at 131° , and has not lost all acid properties, although they have been much weakened by replacing the bromine atom by the basic radical $\text{C}_6\text{H}_5\text{NH}$. It cannot form an ammonium salt, but

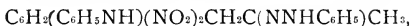
the sodium salt can be easily obtained in alcoholic solution, and on analysis gave a number corresponding to the formula



It is completely decomposed by water, but dissolves in alcohol with a brown color.

Both these ketones, therefore, show stronger acid properties than desoxybenzoine $\text{C}_6\text{H}_5\text{COCH}_2\text{C}_6\text{H}_5$, the metallic compounds of which, according to Victor Meyer,¹ could not be isolated; we are inclined to ascribe this to the presence of the nitro groups in the phenyl, which would heighten its acid-producing power, but it may also be due in part to the fact that these ketones contain the acetyl group, which, as Claisen and Ehrhardt² have pointed out, has a greater influence in producing acidity than the benzoyl radical contained in desoxybenzoine.

The hydrazone of the anilidodinitrobenzylmethylketone,



was also prepared, and melted at 140° .

The full details of the work will be found in the remainder of the paper.

Preparation of Tribromdinitrobenzol.

The method used by us for preparing tribromdinitrobenzol differs from that formerly in use only in certain details, but, as careful attention to these details insures a purer product at much less expense of time and labor, we have thought it best to give a full account of our mode of procedure.

To make the tribromaniline, 60 grams of aniline were dissolved in dilute hydrochloric acid, and, the solution having been made up to a volume of about 3 liters, a rapid stream of air saturated with bromine vapor was sucked through it by means of a Bunsen pump, until the liquid assumed a distinct yellow color. The precipitate of tribromaniline was then removed by straining through cheese-cloth, and washed with a stream of common water until free from acid, when the greater part of the water was squeezed out with a screw press, and the product thoroughly dried on a steam radiator. In this way a quantitative yield of the tribromaniline was obtained, and it was free from colored by-products.

¹ Ber. d. chem. Ges. 21, 1291 (1888).

² Ber. d. chem. Ges. 22, 1019 (1889).

In order to convert the tribromaniline into tribrombenzol, 50 grams of it, after being pulverised, were dissolved with the aid of heat in about 300 cc. of common alcohol, and a concentrated aqueous solution of 21 grams of sodic nitrite poured in slowly, but not in successive portions. The hot mixture was then acidified with dilute sulphuric acid, and allowed to stand over night, when it was filtered, and the precipitate washed with hot water to remove the sodic sulphate and leave the tribrombenzol. An additional quantity of this was obtained by concentrating the alcoholic filtrate, when it separated as an oil, that solidified on standing, and was then crystallised from alcohol. The yield was nearly quantitative, as 45.50 grams of tribrombenzol were obtained instead of the 47.77 required by the theory, that is 95 per cent. When made by this method, the tribrombenzol was usually pure enough to be nitrated directly in spite of its brownish color.¹

To convert the tribrombenzol into the dinitro compound, 25 grams of it were added to 100–120 grams of nitric acid² of specific gravity 1.52 (made from potassic nitrate and sulphuric acid in the laboratory), warmed gently until the solid had dissolved, and allowed to stand about two hours, when the tribromdinitrobenzol crystallised out in large white prisms. The yield was essentially quantitative.

Bromdinitrophenylacetacetic Ester,
 $\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)_2\text{CH}_2\text{COCHCOOC}_2\text{H}_5.$

Preparation.—This substance was made by the action of an alcoholic solution of sodium acetacetic ester on a benzol solution of the tribromdinitrobenzol in the proportion of about four molecules of the former to one of the latter. For this purpose 15 grams of tribromdinitrobenzol were dissolved in about 150 cc. of benzol, and mixed with 20 grams of acetacetic ester previously treated with 3 grams of sodium dissolved in about 150 cc. of absolute

¹ The amount of sodic nitrite used in the process described above (two molecules of nitrite to one of the base) is twice that required by the theory, but we have found that this large excess was necessary to bring all the tribromaniline into the reaction. When a smaller amount of nitrite was used, the product was much less pure, as shown by its lower melting point; it was necessary in this case to distil it from a little retort, and crystallise several times from alcohol, to obtain pure tribrombenzol. The crystals obtained on evaporating the alcoholic mother liquors, which made up about two-thirds of the entire amount, were distilled with steam, pushing the distillation as rapidly as possible, when tribrombenzol passed over, and tribromaniline was left in the retort; but all this tedious purification can be avoided by using the excess of nitrite recommended above.

² This Journal 9, 350 (1887).

alcohol. At first there was very little change of color, but on standing at ordinary temperatures the liquid turned first yellow and then red (whereas with malonic ester the red color appeared instantaneously). In order to complete the reaction, the mixture was heated on the steam-bath for about one hour, at the end of which time it had become nearly black, and a considerable precipitate of sodic bromide had formed. It was then mixed with from one and a half to two liters of water, and the reddish benzol solution, which was precipitated, removed from the dark red aqueous liquid; the latter was then acidified with dilute sulphuric acid, taking care to avoid a large excess; this decomposed the red sodium salt of the new substance, which was set free in the form of a yellowish oil, and extracted by shaking the liquid with ether twice. On distilling off the ether a dark reddish brown oil was left, which, when cold, was treated with very little alcohol, and upon stirring became filled with crystals, the quantity of which increased on standing for twelve or more hours. When the quantity of the crystals did not increase further, the pasty mass was sucked out on the pump, first adding a little alcohol, if necessary, and by washing with a small quantity of cold alcohol all the very soluble red oil was removed from the crystals, which were nearly or quite insoluble in cold alcohol, and were next purified by crystallisation from hot alcohol until they showed the constant melting point 96° . An additional quantity of the substance can be obtained from the benzol solution by distilling off the benzol and treating the residue with sodic hydrate and a little alcohol, which convert the new substance into its sodium salt, and this can be removed from the unaltered tribromdinitrobenzol by washing with water; when the wash-waters were acidified, and the precipitate purified in the same way as the main portion, the substance was dried *in vacuo*, and analysed with the following results:

I. 0.2683 gram of the substance gave on combustion 0.3788 gram of carbonic dioxide, and 0.0748 gram of water.

II. 0.2512 gram of the substance gave 16.7 cc. of nitrogen at a temperature of 22° and a pressure of 759.7 mm.

III. 0.2067 gram of the substance gave, according to the method of Carius, 0.1041 gram of argentic bromide.

IV. 0.2141 gram of the substance gave 0.1059 gram of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2CH_3COCHCO_2C_2H_5$.	I.	II.	Found. III.	IV.
Carbon	38.41	38.50
Hydrogen	2.93	3.09
Nitrogen	7.47	...	7.33
Bromine	21.33	21.43	21.05

The yield of bromdinitrophenylacetacetic ester, prepared by the method described above, is satisfactory on the whole, the best result being as follows:

15 grams of the tribromdinitrobenzol yielded 6.5 grams of the ester, and 3.1 grams of unaltered tribromdinitrobenzol were recovered, leaving 11.9 grams which had entered into the reaction. 11.9 grams of tribromdinitrobenzol should yield 11.0 grams of bromdinitrophenylacetacetic ester. The actual yield, therefore, was 59 per cent. of the theoretical. In other preparations the yield varied from 54 to 34 per cent., the lowest which was obtained from this process. The yield was not improved by increasing or by diminishing the proportion of acetacetic ester to the tribromdinitrobenzol. In our first preparations the reaction was allowed to run in the cold, as an experiment, in which the mixture had been heated less than one hour, seemed to give a very unmanageable product; in this case, however, the yield was very much less than that obtained by the process described above, in which the mixture was heated one hour.

In order to throw light on the way in which the reaction runs, we determined the amount of bromide of sodium formed in two preparations as follows:

I. 12 grams of tribromdinitrobenzol yielded 4.43 grams of bromine in the form of sodic bromide.

II. 12 grams of tribromdinitrobenzol yielded 4.40 grams of bromine in the form of sodic bromide.

If two atoms of bromine are removed from each molecule by this reaction, 12 grams of tribromdinitrobenzol would lose 4.74 grams of bromine.

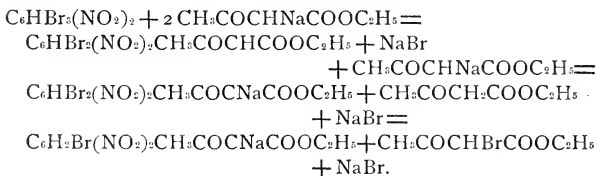
Percentage of bromine removed as sodic bromide,—

I.	II.
93.5	93.0

From this it appears that all the bromine removed from the tribromdinitrobenzol is finally in the state of sodic bromide, as the slight loss of 7 to 6.5 per cent. is not greater than would be

expected when it is considered that the aqueous solution containing the sodic bromide was shaken out twice with ether. These determinations show also that in these cases the whole of the tribromdinitrobenzol entered into the reaction, and, in fact, none of it could be found unaltered in the products of these two preparations; but this was not always the case, as, for instance, in the preparation described on page 169.

The full explanation of the reaction, however, was to be found in the study of its secondary product, the red oil removed from the crystals by washing with cold alcohol. This, upon long standing exposed to the air, threw down a few more crystals of bromdinitrophenylacetacetic ester, which would raise the yield a little above that given, but the amount obtained in this way was very small. The oil, after no more crystals could be obtained from it, was distilled under diminished pressure and yielded some acetacetic ester, leaving in the flask a tarry mass which has shown no signs of giving crystals even after long standing. This part of the work therefore was not carried further, as from the formula of the ester and the removal of all the bromine as sodic bromide there can be no doubt that the reaction with acetacetic ester runs in the same way as that with malonic ester, and in this latter case the reaction has been fully explained.¹ Reasoning on this analogy, the following reactions may be taken as expressing what takes place in the formation of the bromdinitrophenylacetacetic ester.



The bromacetacetic ester being afterward attacked either by a molecule of sodium acetacetic ester or by sodic hydrate.

The only question with regard to these reactions, which might arise, would be due to the fact that only a little over 50 per cent. (59 per cent.) of the ester was obtained, which might lead to the hypothesis that nearly half of the tribromdinitrobenzol went to form another substance; but this objection is removed by the fact

¹ This Journal 12, 15 (1890).

that in another analogous case as much as 80 per cent. of a corresponding ester has been found. We consider, therefore, that the missing 41 per cent. of the ester remained dissolved in the oily secondary product, but should state, on the other hand, that upon treating the oil with sulphuric acid of specific gravity 1.44 in hopes of decomposing the secondary products and converting the bromdinitrophenylacetacetic ester into bromdinitrobenzylmethylketone, we obtained nothing but black tarry substances, from which no substance fit for analysis could be obtained.

Properties.—The bromdinitrophenylacetacetic ester crystallises well, usually in forms looking like a rhombohedron with a very acute angle, less frequently in prismatic forms, which are twinned on a central line parallel to their longer axis, the termination being in shape either like a simple gable, or one with a notch in its point. The crystals show a great tendency to twin, or group, often in forms like those of frost, and are sometimes from 2 to 3 mm. long. The substance has a yellow color of about the shade of potassic chromate, which is characteristic, as the corresponding malonic compound is nearly white. Heckmann¹ has observed a similar deep yellow color in the orthoparadinitrophenylacetacetic ester. It melts at 96°; is very slightly soluble in water, rather more so in hot than in cold; essentially insoluble in ligroine; not very soluble in cold alcohol, but freely in hot; if anything less soluble in methyl than in common alcohol both cold and hot, but the solubility is much greater in the hot methyl alcohol than in the same solvent when cold; tolerably soluble in carbonic disulphide, or ether; soluble in glacial acetic acid; and freely in benzol, chloroform, or acetone; from ether, benzol, or chloroform it is deposited as an oil. The best solvent for it is hot alcohol. Strong sulphuric acid does not act upon it in the cold, but when warm dissolves it, forming a slightly yellowish solution. Strong hydrochloric acid has no action with it in open vessels, even if heated. The decomposition of the substance by these two acids under proper conditions is described later in this paper. Strong nitric acid has no action on it in the cold, but dissolves it when warm; there is, however, no marked change of color, in which respect this substance shows a striking difference from the bromtrinitrophenylmalonic ester, but resembles the bromdinitrophenylmalonic ester.

The bromdinitrophenylacetacetic ester shows marked acid

¹ Ann. Chem. (Liebig), 220, 133.

properties, as was to be expected from the position of one of its hydrogen atoms upon a carbon adjacent to an acetyl, a carboxyl-ester, and a phenyl group, the latter rendered still more efficient by the presence of two nitro groups, and also from the acid properties of the corresponding malonic compound. Aqueous sodic or ammoniac hydrate dissolves it, forming a red solution of the corresponding salt; an aqueous solution of potassic carbonate acts upon it in the same way, giving, however, a somewhat fainter color, but, if alcohol is added to the solution, it turns at once dark red; acid sodic carbonate in aqueous solution gives a very faint red color, which is much intensified by addition of alcohol to the solution. The red solution of the ester in ammoniac hydrate is decomposed by heating, or even by exposure to the air at ordinary temperatures, and we were not able to obtain a solution which did not smell of ammonia, even when a large excess of the ester was used; it is evident, therefore, that its ammonium salt is very unstable. We have, however, tried the action of a solution prepared from an excess of the ester and ammoniac hydrate with various reagents, and found the following characteristic reactions.

Magnesium or Calcium salt, heavy flocculent precipitate of the color of chrome yellow.

Strontium salt, a less heavy precipitate of a redder color.

Barium salt, a still smaller precipitate, also reddish.

Zinc salt, a pale yellow precipitate.

Cupric salt, a pale yellow precipitate.

Lead salt, a dark yellow precipitate.

Silver salt, a yellowish white precipitate.

The most striking thing about these salts is that the calcium salt is less soluble than that of strontium, and this less soluble than the barium salt. Bischoff¹ has observed a similar peculiarity in the salts of orthonitrobenzoylmalonic ester, and we have found it in the salts of bromtrinitrophenylmalonic ester.

With aniline the bromdinitrophenylacetacetic ester gave only a waxy yellow mass, from which there seemed little chance of obtaining a substance in a state fit for analysis. We have, therefore, abandoned the further study of this reaction, in which undoubtedly the aniline acted on the acetacetic ester radical as well as on the bromine in the benzol ring. That this bromine had been removed we proved by detecting aniline bromide among the products of the reaction.

¹ Ann. Chem. (Liebig) 251, 362.

Sodium Salt, $C_6H_2Br(NO_2)_2CH_3COCNaCOOC_2H_5$.

In the earlier portions of our work on the bromdinitrophenyl-acetacetic ester and allied bodies the determination of the composition of the salts was of the greatest importance, as this was the only experimental method which we had found for deciding between the formulas,

- I. $C_6H_2Br(NO_2)_2CH_3COCHCOOC_2H_5$,
- II. $C_6HBr(NO_2)_2CH_3COCCOOC_2H_5$.

This, at present, is no longer the case, as the discovery of acetylen-tetracarbonic ester or tartronic acid as a secondary product in the formation of the corresponding malonic compounds can be explained only if a formula similar to I is adopted, and the easy conversion of bromdi- (or tri-) nitrophenylmalonic ester into the corresponding toluol compound also could hardly be brought into harmony with a formula like II. No similar proof has been applied to the acetacetic compound, it is true; but when the close resemblance between this and the malonic compounds is considered, there can be no doubt that they are similarly constituted. The composition of the sodium salt therefore becomes of secondary importance, and this is fortunate, as we have not succeeded in preparing it in a state of purity sufficient to decide between the salts derived from formulas I and II, although our analyses leave no doubt as to its composition, if the first formula is adopted as correct.

The salt was prepared by adding to a solution of the bromdinitrophenylacetacetic ester in absolute alcohol a solution of sodic hydrate or ethylate also in absolute alcohol, taking care that the ester was in decided excess. The deep red alcoholic solution thus obtained was evaporated rapidly to dryness in a narrow beaker sunk throughout its whole height in a water-bath, some ether having been added previously in order that its vapor might protect the solution from the carbonic dioxide of the air until the alcohol began to boil. The excess of ester was washed out of the dry residue with benzol, and the salt dried at 100° , and analysed with the following results:

- I. 0.2102 gram of the salt gave after treatment with sulphuric acid 0.0361 gram of sodic sulphate.
- II. 0.2056 gram of the salt gave 0.0407 gram of sodic sulphate.
- III. 0.2531 gram of the salt gave 0.0390 gram of sodic sulphate.

	Calculated for $C_6H_2Br(NO_2)_2CH_2COCH_3NaCO_2C_2H_5$.	I.	Found. II.	III.
Sodium	5.79	5.56	6.41	4.99

It is evident from these results that the method of preparation is unsatisfactory, and we ascribe this to the action of the sodic hydrate (or ethylate) on the bromine, and perhaps also on the acétacetic radical, as, when these two sources of error were removed by using the anilidodinitrobenzylmethylketone, an excellent result was obtained. Bad as these analytical results are, they show that the salt contains but one atom of sodium, and therefore must have the formula which we have ascribed to it.

Properties.—The sodium salt of the bromdinitrophenylacetacetic ester forms a brick-red amorphous mass, easily soluble in water, alcohol, or ether, but insoluble in benzol. Much less freely soluble in a solution of sodic hydrate than in water. Strong nitric acid decomposes it, giving apparently the unaltered ester.

Bromdinitrobenzylmethylketone (Bromdinitrophenylacetone),
 $C_6H_2Br(NO_2)_2CH_2COCH_3$.

This substance can be made from the bromdinitrophenylacetacetic ester by the action of dilute sulphuric acid in open vessels, or of strong hydrochloric acid in sealed tubes. The method of preparation which gave us the best results was as follows: 2 to 2.5 grams of bromdinitrophenylacetacetic ester were boiled with about 200 cc. of sulphuric acid of specific gravity 1.44, boiling point 132° , in a flask with a return condenser, until all the solid was dissolved, which took usually from one hour to an hour and a half. The yellow solution was then allowed to cool, when it deposited a heavy white flocculent precipitate, which was increased in quantity by diluting largely with water; it was filtered out, and after thorough washing with water was purified by crystallisation from alcohol until it showed the constant melting point 112° – 113° , when it was dried at 100° for analysis. If the ester used in this process was not perfectly pure, a tarry impurity was formed which could be removed only with great difficulty; the best plan in such a case was to wash the product with a small quantity (20–30 cc.) of benzol, which dissolved the ketone more readily than its impurity, but even after this treatment tedious crystallisation from alcohol was necessary to obtain a pure substance.

The formation of this substance by heating the bromdinitro-

phenylacetacetic ester with hydrochloric acid is not a good method of preparing it, because the process must be carried on in sealed tubes, and also because the product is apt to be contaminated with the tarry impurity just mentioned; but as it throws light on the reaction which takes place, we will describe it briefly: 1 gram to 1.5 gram of the ester was sealed in a tube with 20-30 cc. of pure strong hydrochloric acid, and heated from 130°-150° for two or three hours. Upon opening the tube a gas was evolved which burned with a smoky green-bordered flame (ethylchloride), and also contained carbonic dioxide, as shown by its giving a precipitate with lime-water. The contents of the tubes consisting, in addition to the acid liquid, either of tufts of brownish acicular crystals, or a brown oily semi-solid mass, were poured into a large volume of cold water, and the insoluble portions purified as already described.

The following analyses were made in part with substance prepared by the hydrochloric acid process, and in part with that made with sulphuric acid:

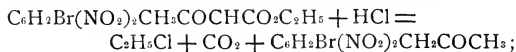
I. 0.2312 gram of the substance gave on combustion 0.3005 gram of carbonic dioxide, and 0.0546 gram of water.

II. 0.1638 gram of the substance gave 14 cc. of nitrogen at a temperature of 23° and a pressure of 755 mm.

III. 0.1862 gram of the substance gave, according to the method of Carius, 0.1173 gram of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2CH_2COCH_3$.	I.	Found. II.	III.
Carbon	35.64	35.44
Hydrogen	2.31	2.62
Nitrogen	9.24	...	9.57	...
Bromine	26.40	26.81

It is evident from the analyses and observations given above that the reaction with hydrochloric acid runs as follows:



and that the reaction with sulphuric acid must be similar. We had expected that bromdinitrophenylacetic acid would be formed also by these processes, but after a most careful search for it not a trace could be detected; and as its properties are so striking that we could not have overlooked it, the conclusion is forced upon us

that the reaction consisted only in the formation of the ketone. This result is the more remarkable because Heckmann¹ obtained from the orthoparadinitrophenylacetacetic ester by treatment with sulphuric acid of about 10 per cent. exclusively the dinitrophenyl-acetic acid without a trace of the corresponding ketone. As the presence of bromine in our compound could hardly have caused such a great difference in the action of the sulphuric acid, we infer that it must have been caused by the difference in strength of the sulphuric acid, Heckmann's containing about 10 per cent. of H_2SO_4 , while ours contained 54 per cent. This inference will be tested by experiment in the coming year.

Properties.—The bromdinitrobenzylmethylketone crystallises from hot alcohol by cooling in white rectangular plates, often with a right-angled notch in one corner, sometimes also in plates with parallel sides and a deep notch in each end, which makes them look like reels. If crystallised by the evaporation of its alcoholic solution, it forms cylindrical tufts of needles looking like spires of moss, or much branched forms resembling certain seaweeds. Both the plates and the branching needles commonly occur together. It melts at 112° – 113° and is essentially insoluble in ligroine; nearly insoluble in cold water, more soluble in hot, but still very sparingly; slightly soluble in ether, carbonic disulphide, benzol, or methyl alcohol, its solubility in the last two solvents is increased by heat; tolerably soluble in ethyl alcohol in the cold, freely when hot; ethyl alcohol dissolves it more freely than methyl alcohol; tolerably soluble in glacial acetic acid; soluble in chloroform; and freely soluble in acetone. Hot alcohol is the best solvent for it. Strong sulphuric acid has no action on it in the cold, but when warmed dissolves it, forming a colorless solution from which water precipitates the ketone essentially unaltered, although it appears at first in spherical groups of thickly set radiating needles, a form in which it is also obtained sometimes when prepared by the action of sulphuric acid on bromdinitrophenylacetacetic ester, but these crystals are converted by crystallisation from alcohol into the rectangular plates described above. Strong nitric acid acts like strong sulphuric acid.

The bromdinitrobenzylmethylketone has well marked acid properties, and in this respect far surpasses the desoxybenzoine from which according to Victor Meyer² no sodium compound

¹ Ann. Chem. (Liebig) **220**, 134.

² Ber. d. chem. Ges. **21**, 1291 (1888).

could be isolated. In alcoholic solution the ketone gives a dark purplish red color with sodic hydrate or ethylate. Aqueous ammoniac hydrate gives only a slight red color with it, which is increased by warming for a short time, and still more by the addition of alcohol, but the color disappears if the heating is long continued. Aqueous potassic carbonate gave no action, but on the addition of alcohol a very dark purplish red solution of the salt. Acid sodic carbonate had no action in aqueous solution, and only very slight on addition of alcohol. The dark red alcoholic solution of the ammonium or sodium salt, if made with an excess of the ketone, is decomposed by water, giving a white precipitate of the ketone. The decomposition is not complete, however, as the liquid retains a pale red color. In the presence of an excess of sodic hydrate, the salt is much more stable. An attempt was made to study the action of the pale red aqueous solution of the ammonium salt with various reagents, but no characteristic precipitates were obtained, probably on account of the small amount of salt left in solution.

We tried also to prepare and analyse the sodium salt, the method being that adopted for the sodium salt of the bromdinitrophenyl-acetacetic ester; but the results of the analyses came much too high, 9.73 and 8.64 per cent. of sodium, instead of the 7.07 per cent. required by the formula. The reason for this difference is that the sodic hydrate or ethylate removed a portion of the bromine from the ketone, and the benzol, dissolving the organic product, left the sodic bromide formed with the salt of the ketone, as was proved by dissolving the salt in water and acidifying with nitric acid, when, after removing the precipitate by filtration, argentic nitrate gave a heavy precipitate of argentic bromide in the filtrate. We accordingly turned our attention to the anilidoketone, our work on which is described later in this paper. We add here the *properties* of the *sodium salt of bromdinitrobenzylmethylketone*. It is a purplish black amorphous substance, very easily soluble in alcohol, forming a dark claret-red solution, the color of which is so much more purple than that of the salt of the corresponding acetacetic ester that the two substances can be easily distinguished in this way; it is decomposed almost, but not quite, completely by water, and is insoluble in benzol.

The ketone is a decidedly reactive substance. When treated with aniline, it gives aniline bromide and the anilidodinitrobenzyl-

methylketone, which is described later. With phenylhydrazine it appears to form a hydrazone, but at the same time the bromine was removed from the benzol ring, so that the product seemed to be a phenylhydrazidohydrazone. It was free from bromine, and exploded when touched with a hot wire; but as its purification offered considerable difficulties, we did not try to investigate it thoroughly. The ketone seems to react in the same way with hydroxylamine, since in this case also bromine seemed to be removed; but as the product did not have inviting properties, we have not attempted to isolate the oxime. If the ketone is dissolved in chloroform, the solution mixed with bromine, and allowed to stand at ordinary temperatures, hydrobromic acid is given off in considerable quantity, and a new substance melting at least 10° higher than the original is formed, which will be investigated in this laboratory next term. It is a curious fact that, if a solution of the ketone in carbonic disulphide instead of chloroform was treated with bromine, no hydrobromic acid was given off, so far as we could find.

Anilidodinitrobenzylmethylketone,
 $C_6H_2(C_6H_5NH)(NO_2)_2CH_2COCH_3.$

This substance is prepared easily by the action of aniline on the bromdinitrobenzylmethylketone. The substances were mixed in the proportion of one molecule of the ketone to two of the base, and the mixture, which had a bright red color, warmed for 15 to 20 minutes on the water-bath. The product was then freed from the aniline bromide and any slight excess of aniline by washing with water to which a little hydrochloric acid was added, the residue, which contained no bromine, purified by crystallisation from hot alcohol till it showed the constant melting point 131° , dried at 100° , and analysed with the following result:

0.1980 gram of the substance gave 23.2 cc. of nitrogen at a temperature of 25° and a pressure of 771.2 mm.

	Calculated for $C_6H_2C_6H_5NH(NO_2)_2CH_2COCH_3.$	Found.
Nitrogen	13.33	13.26

Properties.—The anilidodinitrobenzylmethylketone forms, when crystallised from alcohol, bright yellow groups of curving needles, which look at first like two heads of palm-trees cut off at the point where the leaves grow out of the trunks and put with the stumps.

together. As more crystals are formed the groups develop into irregular chestnut-burs. It melts at 131° ; is essentially insoluble in ligroine; nearly insoluble in cold water, slightly soluble in hot, forming a pale yellow solution; slightly soluble in ether; soluble in cold ethyl or methyl alcohol, more freely in either of these solvents when hot; soluble in benzol, carbonic disulphide, or glacial acetic acid; freely soluble in chloroform or acetone. Alcohol is the best solvent for obtaining crystals. Strong sulphuric acid dissolves it, forming a brown solution. Strong nitric or hydrochloric acid dissolves it with a yellow color, but it is very slightly soluble in hydrochloric acid.

The acid properties of this substance are much less marked than those of the corresponding bromine compound, as was to be expected from the substitution of bromine by the basic radical C_6H_5NH . Aqueous sodic hydrate has no action on it in the cold, and but slight when warm, but if alcohol is added a brownish red solution of the sodium salt is obtained. Ammonic hydrate, on the other hand, could not be made to act on it, even by warming in presence of a large excess of alcohol. Potassic carbonate in aqueous solution had no action on it, either cold or hot, but gave a very slight action when a large quantity of alcohol was added. The behavior of the solution of a soluble salt with various reagents could not be studied, as the alcoholic solution of the sodium salt was decomposed completely by diluting it with water. But in spite of these weaker acid properties we selected the sodium salt of this substance for analysis, as there was no danger of a decomposition of this ketone by the alkali used, such as had prevented us from getting good results with the corresponding bromine compound. For the same reason the hydrazone for analysis was prepared from this substance instead of from the bromdinitrobenzylmethylketone.

Sodium Salt of Anilidodinitrobenzylmethylketone,
 $C_6H_2(C_6H_5NH)(NO_2)_2CHNaCOCH_3$.

This substance was prepared by adding an alcoholic solution of sodic ethylate to an excess of the ketone also dissolved in absolute alcohol. The narrow beaker containing the mixture, after the addition of a little ether, was sunk to its rim in a steam bath. In this way, at first the ether, and later the alcohol vapor, prevented the carbonic dioxide of the air from acting on the salt during the

evaporation. The dry residue was thoroughly washed with benzol to remove the excess of the ketone, and the salt thus purified dried at 100°, and analysed with the following result:

0.2380 gram of the salt gave after evaporation with sulphuric acid 0.0500 gram of sodic sulphate.

	Calculated for	Found.
	$C_6H_2(C_6H_5NH)(NO_2)_2C_3OH_4Na.$	
Sodium	6.82	6.80

Properties.—A brownish black mass, soluble in alcohol, giving a much browner solution than any of the other salts described in this paper, so that it could be recognised with ease by its color. It is decomposed at once by water, the brown alcoholic solution being turned yellow and turbid. It seems to be nearly or quite insoluble in ether, and is insoluble in benzol.

Anilidodinitrobenzylmethylketonehydrazone,
 $C_6H_2(C_6H_5NH)(NO_2)_2CH_2C(N_2HC_6H_5)CH_3.$

This substance was made by warming for 20–30 minutes on the water-bath in an open dish a mixture of anilidodinitrobenzylmethylketone with phenylhydrazine in the proportion of one molecule of the former to about one and a half of the latter, so as to have a decided excess of the hydrazine. At the end of this time the mixture had changed from yellow to dark carmine red, and solidified to a tarry mass, which was crystallised once or twice from alcohol to bring it into a finely divided state, and washed with water containing a little hydrochloric acid till the excess of phenylhydrazine had been removed, after which it was boiled with alcohol on the water-bath, and while boiling enough benzol added cautiously to effect the solution; the mixture was then boiled for about a minute, when upon cooling crystals were deposited, and this crystallisation was continued until the substance showed the constant melting point 140°, when it was dried at 100°, and analysed with the following result:

0.2177 gram of the substance gave 32.5 cc. of nitrogen at a temperature of 22° and a pressure of 763 mm.

	Calculated for	Found.
	$C_6H_2(C_6H_5NH)(NO_2)_2CH_2C(N_2HC_6H_5)CH_3.$	
Nitrogen	17.28	16.97

Properties.—The hydrazone crystallises well in reddish brown scales, resembling strongly in general appearance the officinal ferric

citrate. The scales often reach a diameter of 3 to 4 millimeters. Under the microscope plates were observed which seemed to belong to the monoclinic system, but with these were very irregular forms, often serrated on one or both sides, or irregularly diamond-shaped with re-entering angles, usually either grouped in radiating masses, or in crowded branching collections of thick needles. It melts at 140° , but, as it seems to be slightly decomposed by crystallisation, it was difficult to determine the melting point with perfect exactness. It is essentially insoluble in ligroine or cold water; very slightly soluble in boiling water or in ether; slightly soluble in cold alcohol, more soluble, but still not freely, in hot; more soluble in methyl than in ethyl alcohol; slightly soluble in cold glacial acetic acid, freely in hot; soluble in cold benzol or carbonic disulphide, freely soluble in these solvents when hot; easily soluble in chloroform or acetone, even in the cold. As the benzol solution deposits the substance in a viscous state, it is best to crystallise from a mixture of alcohol and benzol, as described above in speaking of its preparation. Strong hydrochloric acid has no action upon it. Strong nitric acid seems to decompose it, dissolving a little of the product. Strong sulphuric acid dissolves it with a yellowish brown color.

Neither sodic or ammoniac hydrate, nor potassic carbonate, nor acid sodic carbonate, gives any action with it in aqueous solution, hot or cold, or even on addition of alcohol; but if it is warmed with sodic hydrate, water, and alcohol, a little dissolves with a brown color, and if a drop of sodic hydrate is added to an alcoholic solution, a dark brownish red solution is formed, which is decomposed by water. It may be, therefore, that the substance has not lost completely the power of forming salts, but it is on the whole more probable that the salt is derived from anilidodinitrobenzylmethylketone formed by the action of the sodic hydrate on the hydrazone, as the action was certainly accompanied by decomposition, since there was a smell of isocyanphenyl, and the hydrazone could not be recovered from the solution in sodic hydrate.

The study of the bromdinitrobenzylmethylketone will be continued in this laboratory.

REVISION OF THE ATOMIC WEIGHT OF GOLD.

BY J. W. MALLET, F. R. S.,

Professor of Chemistry in the University of Virginia.

[Continued from page 99.]

Fifth Series of Experiments.

In these experiments an attempt was made to determine the ratio between the weights of metallic gold and metallic silver deposited by the passage of one and the same electric current successively through solutions of the two metals. The simplicity and accuracy with which the direct weighings may be made seemed to present decided advantage, but various difficulties were encountered, and, after the expenditure of a very large amount of time and labour upon the method, it cannot be said, on the whole, to have satisfied me with its results.

While taking due note of the recent literature on the subject of the quantitative electro-deposition of metals from their solutions, especially the reports of work by A. Classen,¹ Lord Rayleigh and Mrs. Sidgwick,² Dr. Gore,³ Thos. Gray,⁴ and W. N. Shaw,⁵ the author of the present paper made for himself a somewhat extended preliminary examination of the effect of varying conditions on such depositions, so far at least as seemed to be required for his immediate purpose.

The general arrangement of apparatus adopted consisted of a horizontal strip, 4 mm. thick, of vulcanite, or hard vulcanised india-rubber, about 26 cm. long by 3 cm. wide, near each end of which and in the middle of the width were two small holes, through which passed short bits of brass rod, each having attached to it above a binding screw, and below a forceps-like clip, which could be opened by pressure on two little outside studs, but closed firmly, on release of this pressure, by the elasticity of the metal. In these clips were supported the plates of metal to be immersed in the electrolysed solutions, and to serve as anode and cathode terminals respectively, there being two pairs of such plates, one pair near each end of the vulcanite strip, with

¹ A. Classen, *Quantitative chemische Analyse durch Electrolyse*, 2te Aufl., Berlin, 1886.

² *Phil. Trans.*, 1884, 411.

³ *Nature*, March 16, 1882; Feb. 1 and Feb. 15, 1883.

⁴ *Phil. Mag.*, Nov. 1886, 389; and March, 1888, 179.

⁵ *Ibid.*, Feb. 1887, 138.

four corresponding binding screws. The electric current passed from the first binding screw through one of two metallic solutions—as, for instance, that containing gold—between the first pair of plates, consisting of the same metal as that in this solution, then from the second binding screw to the third (at the other end of the vulcanite strip) by a stout copper wire above, and then through the second of the two solutions—as, for instance, that of silver—between the second pair of plates, consisting again of the same metal as that in the solution in which they were immersed, thus reaching the fourth and last binding screw, the first and last binding screws being, of course, connected by wires with the terminals of the galvanic cells used to develop the current. Fig. 3 shows the disposition in question. The source of the electric

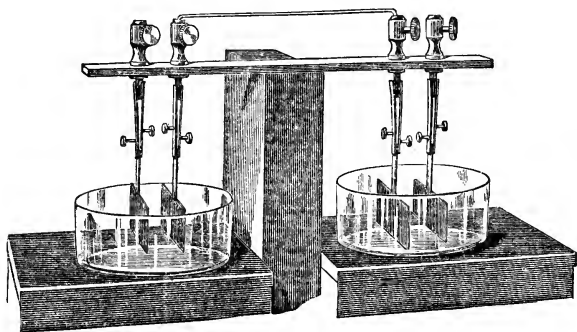


FIG. 3.

current was for the most part galvanic cells of the Meidinger pattern, but in some of the experiments small Daniell cells, and also a Clamond thermo-electric battery, were used. The lower parts of the clips were heavily electroplated with the same metal as that in the solution to which they respectively belonged, in order to avoid any risk of contamination of the solution, in case there should be spattering or accidental immersion, even for a moment, of any part of the clip.

It was decided to place the plates vertically in the liquids, but to make the vertical height small in proportion to width, so as to preserve as far as possible a uniform condition of the solution in

depth. The form adopted for the plates was that of Fig. 4, the shaded part of the surface being coated with hard paraffine, with a view to preventing the strip by which the anode plate was sus-

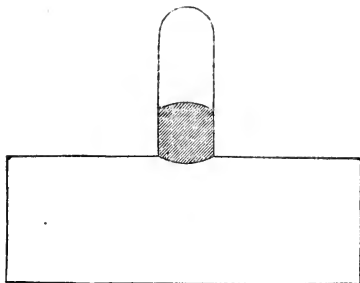


FIG. 4.

ended from its clip being cut across by solvent action at the surface of the liquid. This coating of paraffine was put on after the plates were first weighed, and carefully removed before the second weighing. The four plates for each experiment were of equal size as to length and breadth; in most of the experiments the immersed surface (of one side) measured about 25 square centimeters, though in some cases plates of double this size were used. The thickness was the same for plates of the same metal, but those of the different metals to be compared were made to differ in thickness to such an extent as to allow for the different rate of solution to be expected of the anode plate. I was indebted to the kindness of Mr. Eckfeldt, of the Philadelphia Mint, for having plates of "proof" gold and silver specially rolled for me with all necessary precautions as to perfect cleanliness of the rolls etc., so as to obtain the determinate thicknesses desired.¹

¹ Mr. Eckfeldt informed me that his method of preparing the proof silver used for these plates was as follows: "Nitrate of silver from the gold assay parting is, after careful filtering, precipitated with hydrochloric acid, and the chloride of silver, after a thorough washing with pure water, is dried and reduced in the melting pot with pure carbonates of soda and potash and carbon in the shape of wheat flour, the melting being done in a clay crucible. The resulting silver bar is then dissolved in dilute nitric acid, and after standing some time filtered, precipitated, and reduced as before; then remelted with the addition of pure nitrate of potash and borax. This generally gives a bar somewhat brittle (crystalline in fracture). It is then remelted, and stirred with a pine stick, and chloride of ammonium added; when the chloride has disappeared the metal is poured. I find this method more satisfactory than any other I have tried."

By heating in a Sprengel vacuum I found traces of oxygen in the rolled silver plates, and extremely minute traces of gas, apparently also oxygen, were likewise obtained from the gold plates, before either had been used.

The middle of the vulcanite strip was supported at a suitable height, so as to allow of equal immersion of the two pairs of plates in their respective solutions, which were contained in small vessels of good hard glass, free from lead. Care was taken to keep the vulcanite strip dry, so that there should be no practical defect of insulation between the two plates of each pair; the necessity for this precaution having been shown in some of the very early preliminary experiments with copper plates, using a wooden supporting strip; some puzzling results being traced back to a little accidental moistening with sulphate of copper solution of the part of the strip between one pair of plates, while those of the other pair were well insulated as to the strip from which they hung.

In all the experiments the two pairs of plates, previously ignited in the Sprengel vacuum, cooled and weighed, were placed in position in the clips, the distance between the parallel surfaces of the plates of each pair being the same, and in most of the experiments measuring about 2.5 cm., and connection was made with the terminals of the galvanic cell or cells used before immersion of the plates in the metallic solutions. All four plates were immersed at the same moment, and at the end of the experiment were in like manner lifted out of the solutions at the same moment, before the current had been broken. They were immediately introduced into one after another of several portions of distilled water before removal from the clips, thorough washing, heating in the Sprengel vacuum, and final weighing.

A preliminary course of experiments was carried out with plates of pure electrottype copper (both pairs) in solutions of cupric sulphate, in order to test the effects, if any, of the following differences in the conditions of the two electrolysis cells compared.

1. *Effect of Difference in the Degree of Concentration of the Two Solutions.*—The solution in one of the two vessels in which the plates were immersed being made to contain but one-tenth the proportion of cupric sulphate existing in the other, acidification and all other conditions being the same for both, only a very minute difference was found between the quantities of copper deposited in the same time on the two cathode plates, and the

difference was not invariably in the same direction. The tendency, however, seemed on the whole to be toward a slightly larger amount thrown down from the stronger than from the weaker solution. In every case there was decidedly more copper dissolved from the anode than was deposited on the cathode plate.

2. *Effect of Difference in Acidity of Two Solutions, otherwise of the Same Strength.*—With the same proportion of cupric sulphate in both solutions, one was made to contain but one-tenth as much free sulphuric acid as the other; all other conditions remained the same for both. As before, the difference of result was insignificant, and somewhat variable in direction, with an apparent tendency towards a very slightly greater deposit on the cathode plate in the less acid as compared with the more acid solution. As before, there was in every case a distinctly greater loss of copper from the anode than gain on the cathode plate, especially in the more acid solution.

3. *Effect of Difference in Temperature of the Two Solutions.*—The proportion of cupric sulphate and of free acid being the same for both solutions, and all other conditions the same, one of the two, however, being maintained at 72° , 47° , or 37° C., while the other was at 2° C., thus establishing a difference in temperature of 70° , 45° , or 35° respectively, there was distinctly in every instance rather more copper thrown down on the cathode plate in the colder than in the warmer solution. The loss of weight of the anode plate was always greater than the gain at the cathode, and the difference in this respect was greater in the warmer than in the colder solution.

4. *Effect of Difference in the Size of the Plates.*—All other conditions being the same in both the electrolysis cells, the plates in one were made to present but one-fourth the surface of those in the other, so that the "current density" was proportionally increased in the former. Under these circumstances there was a constant, though but small, difference in the amount of copper deposited on the two cathodes, the quantity being greater on the cathode plate with smaller surface. The tendency seemed to be towards a greater excess of metal removed from the anode over that deposited on the cathode plate in the case of the larger plates, as compared with the smaller.

5. *Effect of Difference in the Distance between the Plates.*—The plates of both pairs being equal in size, and all other condi-

tions being uniform, the plates in one of the two electrolysis cells were placed at a distance apart only one-fifth that intervening between those of the other pair. It was not clear that any constant difference of result could be detected, but the tendency seemed to be rather toward a very slightly greater deposit on the cathode plate in the case in which the plates were farther apart as compared with that in which they were nearer together. There was no recognisable difference in the proportion of metal dissolved off from the anode plate.

Similar experiments were made with two pairs of plates of pure silver, thus checking the results obtained with copper, and contrasting the behavior of one at least of the less chemically alterable metals with that of the more easily alterable copper. It was intended to make a set of similar experiments also with gold plates only, but the available supply of pure gold in the form of rolled plates was not sufficient for the numerous experiments required. The silver solution used was one of potassium argentocyanide, and the substitute for the free sulphuric acid of the copper experiments was an excess of potassium cyanide. The results obtained were essentially similar to those of the copper experiments, the effect of difference in temperature between the two solutions being, however, less decided, and the slight effect of difference in the size of the plates ("density of current") less constant and distinct.

In all the preceding experiments it was found that the most constant results under otherwise similar conditions were obtained by using feeble currents rather than those of greater strength, especially in the case of the silver solutions. There seemed, however, to be a limit to this. On the whole, the most satisfactory results were obtained (both in these preliminary experiments and in those aiming at the atomic weight determination) with currents not exceeding $\frac{1}{100}$ th of an ampère per square centimeter of surface of (one side of) the opposed plates, and in some cases a current but one-fifth of this maximum was used.

Having in view the indications afforded by the preliminary experiments, it was determined to use tolerably strong solutions of the metals to be deposited, with not more than a moderate excess of free acid, or, in the case of the double cyanide solutions, excess of potassium cyanide, to maintain the same temperature in both the electrolysis cells, and to have this temperature as low as

possible (about 2° C.), and to have the plates of the two metals to be compared equal in size, and at equal distances apart, using a weak electric current, and keeping watch over its strength by means of an ordinary hydrogen voltameter in the circuit.

In the actual experiments on the deposition of gold as compared with silver, it was originally proposed to use a solution of potassium auri-cyanide against one of potassium argento-cyanide, with the expectation that 3 atoms of silver would be thrown down for 1 atom of gold. But the first attempts made showed clearly that this reaction could not be obtained. The comparison as to gain in weight of the gold and silver cathode plates gave results leading to an atomic weight for gold impossibly high if the silver deposited were taken to represent 3 atoms, and much too low if it were taken to represent but 1 atom. Hence it appeared that the potassium auri-cyanide had been partially, but not completely, reduced to auro-cyanide by the action of the current, and an intermediate result obtained as to the equivalent quantity of silver between that due to the one or the other gold salt if exclusively present.

A change was therefore made to the auro-cyanide in the preparation of the solution to be electrolysed. A pure form of potassium cyanide was prepared with the aid of alcohol, and carefully tested as to the absence of any metal capable of deposition from the watery solution on electrolysis. Auric chloride was precipitated by ammonia, the fulminating gold, after washing, dissolved in a strong solution of this potassium cyanide with the aid of heat, and the auro-cyanide crystallised out by cooling. The crystals were washed, redissolved in water, aurous cyanide separated from the solution by evaporation with hydrochloric acid, and the crystalline powder after cautious washing again dissolved in potassium cyanide solution, using for the purpose the barely necessary amount of the solvent liquid, but afterwards adding a further quantity, so as to have potassium cyanide in excess. Potassium argento-cyanide was prepared by precipitation of a solution of pure silver in nitric acid with the purified potassium cyanide, washing the precipitate, and re-solution with the aid of the necessary quantity of potassium cyanide, of which finally a moderate excess was added. The solutions of the gold and silver salts were made of equivalent strength, for the most part at the rate of 7 grams of metallic gold for each 100 cc. of solution, and an approx-

imately corresponding amount of silver, taken atom for atom. Both solutions received the same excess of potassium cyanide, generally equal to one-half of that already present in the double salt, but in some of the experiments it was found necessary to add yet more during the electrolysis in order to preserve the purely metallic character of the surface of the plates. As an additional security against admixture of auri-cyanide with the auro-cyanide of the gold solution, it was subjected for some time to electrolysis with unweighed gold plates immersed, these being reversed two or three times in position, just before the introduction of the weighed plates for a quantitative experiment. A number of attempts were made to substitute for the solution of potassium auro-cyanide one of sodium auro-thiosulphate, of potassium or sodium auri-chloride, and of simple auric chloride, in the last two cases employing at the same time a solution of silver nitrate, but these efforts led to no success.

In many of the experiments made with the double cyanide solutions the cathode plates, both of gold and silver, after removal from the electrolysis cells and thorough washing, were found to curl up on being heated, the deposit, which in these cases was rather hard and brittle, swelling up in a remarkable way, with formation and bursting of little blebs or minute bubbles of the metallic surface, and parting off to some extent of the deposit from the original plate underneath. When the heating was carried out in the Sprengel vacuum small but quite appreciable amounts of hydrogen were found to be given off, having been occluded in the metal deposited. It seemed necessary to throw aside the results in all cases in which this condition of the deposit was well marked. Other experiments were vitiated by the gold deposit not being thoroughly compact, and still others by the surface not being clearly metallic, aurous cyanide making its appearance from the solution. It was hoped that in the experiments, free from apparent defect, any irregular behavior of the gold solution at first might be got rid of by continued electrolysis, with reversal of the anode and cathode plates when necessary, until the ratio of gold to silver deposited should become constant; but confidence in this was greatly shaken when an instance occurred, followed afterwards by others, of sudden change in this ratio, attended with much less loss from the anode gold plate than the gain of the opposed cathode

plate, pointing to deposition of gold from the auro-cyanide with simultaneous formation of auri-cyanide in the solution.¹

Altogether but five experiments made in this way yielded results which seemed worthy of being used to determine the atomic weight of gold, and it is of course unsatisfactory to know that these were selected out of a much larger number, mainly because, while not known to be in any way vitiated by apparent defects, they lead to values for the atomic weight in question close to those obtained by other methods and other experimenters. It is possible that this near approach to agreement may merely result from a balance of errors in opposite directions, which, taken separately, would have caused the experiments to be rejected. Some other experiments, under apparently similar conditions, gave figures for the atomic weight differing from those reported by one or two whole units.

These only admissible results are the following :

Experiment.	Character of gold in solution.	Character of gold in plates.	Gold deposited, grams.	Silver deposited, grams.
I.	A, <i>b</i> .	B	5.2721	2.8849
II.	"	"	6.3088	3.4487
III.	"	"	4.2770	2.3393
IV.	"	"	3.5123	1.9223
V.	"	"	3.6804	2.0132

Aside from other difficulties liable to be encountered in carrying out this electrolytic method, the two most important sources of possible inherent error which suggest themselves are the occlusion of hydrogen by the metallic deposit and the instability of the atomicity of gold in the solution electrolysed.

The separation of hydrogen on the cathode plate, whether in bubbles (which may be avoided by proper regulation of the current) or occluded by the metal (which does not seem to be completely avoidable with any current, although the amount of occluded gas was extremely small in a number of my experiments), must be ascribed to decomposition, simultaneous with

¹ Hittorf (Poggendorff, *Annalen*, [4], **16**, 523), in the simultaneous electrolysis of gold and silver solutions, the gold as potassium auri-chloride, obtained results which showed that this metal was deposited at the rate of 1 atom for 3 of silver. Calculating on this basis from his two experiments, the atomic weight of gold comes out = 196.311 and 194.197 ; for silver = 107.66.

In one experiment of my own, using sodium auri-chloride, the result showed that the gold was thrown down for the most part as a triad, but partly as a monad, element.

that of the cyanide of gold, either of water or, more probably, of cyanide of potassium, with secondary action of the potassium on the water. In either case it is by no means clear that the proportion of current giving rise to this liberation of hydrogen can be counted upon as the same in the gold solution and in that of silver, and hence, even though it be fairly assumed that Faraday's principle of equivalent electrolysis by the same current is strictly correct for the *ensemble* of chemical actions in the two cells, the portion of current actually concerned in depositing gold or silver only in each of the respective cells may conceivably not be quite the same, so that the weights of the two metals thrown down may not be strictly equivalent.¹ It was, therefore, deemed important to work with feeble currents, and, while heating all the plates in a Sprengel vacuum before weighing, to reject the results of all those experiments in which the quantity of gas thus discharged amounted to more than the merest trace. But, if the source of error in question still exist at all, it might affect the atomic weight of gold in comparison with that of silver, either by making the former appear higher or lower than the truth.

The source of error most to be feared, however, in connection with the application of this electrolytic method to the determination of the atomic weight of gold, is the uncertainty of having all the gold throughout the process in the form of potassium aurocyanide in the solution, in view of the transition observed to auricyanide during electrolysis, although change in the opposite direction occurs with even greater ease. Each of the two salts appears to admit of electrolytic decomposition, and the presence of any traces of the auri-cyanide, in which the gold has triad character, while the calculation is based on the supposed presence of monad

¹ As bearing on the question of the simultaneous decomposition of two electrolytes in the same solution, the following results may be recorded of an experiment made with a solution of mixed zinc and copper sulphates, with excess of potassium cyanide, the anode plate being of brass and the cathode plate of platinum, and an analysis made of the proportions of the two metals in the anode plate, in the solution as first taken, and in the alloy deposited on the cathode plate and subsequently dissolved off from it by means of nitric acid.

Proportion of copper to zinc.	In the brass anode plate.	In the solution electrolysed.	In the alloy deposited on the cathode plate.
Copper	68.74	13.81	73.34
Zinc	31.26	86.19	26.66
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

Different results would undoubtedly have been obtained by substituting some other metal for one of those taken.

gold only, would, of course, tend to make the atomic weight of the metal appear lower than the truth.

Sixth Series of Experiments.

These experiments consisted merely in the further application of electrolysis to the deposition of metallic gold from a solution of potassium auro-cyanide, comparing the weight of the metal thrown down, however, not with the weight of silver, but with the volume of hydrogen gas liberated by the action of the same current, the object being to thus secure, with an assumed knowledge of the

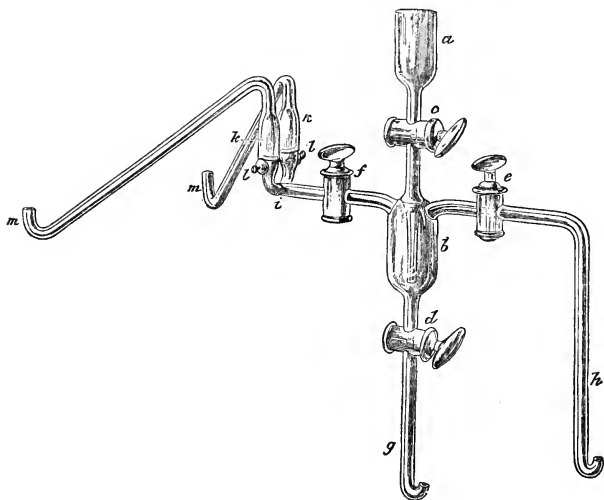


FIG. 5.

density of hydrogen, a direct comparison of the atomic weight of gold with that of the element most generally taken as a basis of the numerical constants in question.

A cell containing the same solution of potassium auro-cyanide as was used in the fifth series of experiments, and having immersed in it a pair of plates of "proof" gold, as already described, was employed for the deposition of the gold. The same current which traversed this cell was passed through a hydrogen voltameter of

special construction,¹ made of glass, in a single piece, the general character of which will be seen from Fig. 5.

When this instrument was to be prepared for use, it was cautiously heated pretty strongly in an air-bath to remove the film of moisture and air from the internal surface, drawing dry air through by means of an aspirator. Clean mercury, previously heated, was then poured in through the funnel *a*, going down to nearly the bottom of the cylindrical vessel *b*, until this vessel—about 30 mm. in diameter and 60 mm. in height—was completely filled, and also the tubes and stopcocks *c*, *d*, *e* and *f*, each of these in succession being opened to allow escape of air, and afterwards closed; *f* was a three-way stopcock, which could either be made to open communication between the parts of the tube on either side of it, or to simply close this tube, or to close this tube and establish communication between the vessel *b* and the outside air through the base of the stopcock; it was in this last-named way that air and surplus mercury were allowed to escape, filling the tube between *b* and *f* with mercury, but not allowing of any of the metal going further along the tube towards *i*. The stopcock *c* was closed, with the tube on which it was situated completely full of mercury, and leaving surplus mercury in the funnel *a*. In filling *b* and its connected tubes care was taken to leave no visible bubbles of air. Pure water mixed with one-twelfth its weight of pure sulphuric acid was boiled for some time in a small flask to expel all dissolved air, keeping up the volume by additions from time to time of water kept boiling in a second flask; the lower turned-up end of the tube *h* was then immersed in the dilute acid, and the lower end of *g* in a cup of mercury; on opening the stopcocks *c* and *d* mercury ran out from *g*, and the dilute acid came in through *h*, filling about half full the cylinder *b*. Closing *d* and *e*, opening *c*, and keeping up a supply of mercury in the funnel *a*, *f* was now turned so as to force out through the base of this stopcock the little mercury in the tube behind it, and fill this tube with the acidulated water. Then *f* was turned so as to allow of this acidulated water being forced on to the bend *i* and into the two little voltameter tubes *k* and *k*, filling these about one-third full. While these tubes were being thus filled the extremities of the delivery tubes *m* and *m* were in communi-

¹ This piece of apparatus—an excellent specimen of skilled glass-blowing—was made, from drawings furnished by me, by Mr. Emil Greiner, of 63 Maiden Lane, New York.

cation with a Sprengel pump, so that they were very nearly exhausted of air. The stopcock *f* having been closed, *e* was opened, and by suitable tilting of the apparatus, and running in of mercury from the funnel *a*, nearly all of the acidulated water from *f* backwards was expelled through the tube *h*. A repetition of the procedure by which the cylinder *b* had been partially filled with acidulated water now served to partially fill it with well-boiled and still hot distilled water to which no acid had been added. The two delivery tubes *m* and *m* were severally detached from the Sprengel pump, after allowing (by a special separate arrangement of tubes with stopcocks) hydrogen to enter one of the two and oxygen the other, and when thus filled the ends of these two tubes were dipped under mercury, and the two platinum wires, *l* and *l*, sealed into the voltameter tubes were connected by the little rings on their outer ends with the terminals of the galvanic cells whence the electric current was to be derived, taking care, of course, to connect to the negative pole the wire of the tube already filled in its upper part with hydrogen, and to the positive pole the wire of the oxygen tube. Viewed from the front, the two voltameter and delivery tubes presented the appearance shown in Fig. 6. The little voltameter tubes *k* and *k* had an external diameter of about 12 mm. and a length of 40 mm. The

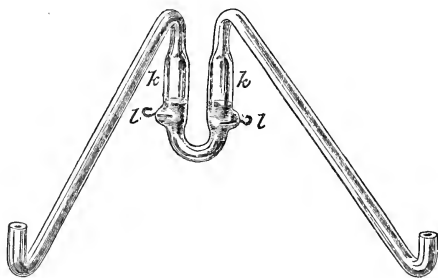


FIG. 6.

platinum wires, *l* and *l*, serving as electrodes were 1 mm. in diameter, and extended beyond the interior surface of the glass (into which they were sealed) for only 3 mm. in length. They could be well covered, and the voltameter tubes filled to one-third their capacity, with only about 2 cm. of the acidulated water.

By careful tilting of the apparatus laterally it was found to be possible to so regulate the pressure of mercury at the ends of the delivery tubes, and therefore the gaseous tension in the two voltameter tubes, that the acidulated water was not forced over from the one to the other, which, had it occurred, would have allowed admixture of the two gases; this required constant watching, however, and there was needed from time to time a little tapping of the apparatus to get rid of the effect of irregular adhesion of the liquid to the walls of the voltameter tubes.

It will be seen that, with the arrangement described, the electrolysis could be effected of acidulated water, thoroughly deprived in advance of dissolved air, and in quantity so small as to be capable of retaining in solution but infinitesimal quantities of the hydrogen and oxygen electrolytically separated. As the decomposition proceeded, the quantity of liquid in the voltameter tubes could be maintained constant by opening the stopcock *c*, with a supply of mercury in the funnel *a*, and then cautiously opening *f*, so as to feed forward a little of the air-free water from the cylinder *b*, thus leaving the proportion of acid unaltered. The surface presented by the platinum wire electrodes was so small as to allow of occlusion of the gases to only an extremely minute extent, and both the hydrogen and oxygen were allowed to escape for some time before any was collected for measurement.

The hydrogen only was collected and measured. I had hoped to apply this form of voltameter to a more exact determination of the relative volumes of hydrogen and oxygen derived from water by electrolysis than is possible with the voltameters of more common construction. But I have not yet seen my way to getting over the difficulties connected with the presence of ozone, hydrogen dioxide, Berthelot's persulphuric acid, or other by-products in the oxygen gas evolved at the positive pole. If this could be accomplished, a useful contribution might possibly be made to the question, revived and worked upon of late by several chemists, of the exact atomic weight of oxygen. The vessel for collecting and measuring the hydrogen, shown in Fig. 7, consisted of a spherical globe of tolerably stout glass, with a capacity of about 250 cm., having a neck of about 1 cm. internal diameter, and 22 cm. long. This neck had etched upon it a simple linear scale of millimeters. At the mouth it was fitted with a well-ground perforated glass stopper, forming part of a glass stopcock with an outer orifice of about 1 mm. bore. The exact capacity of the

whole globe and neck was ascertained by heating it in an air-bath to remove air and moisture condensed on the interior surface, drawing dry air through with an aspirator, then filling the globe with heated mercury, allowing it to cool to an accurately noted temperature, immersing the body of the globe in an outer vessel of mercury so as to prevent extension or flexure of the glass by the weight of the contained metal, filling up to the very mouth with mercury, inserting the stopper with the stopcock open, thus



FIG. 7.

forcing out through its orifice the last of the air, closing the stopcock, removing from the orifice tube, by an iron wire, the drop or two of mercury remaining in it, and then emptying the flask and carefully weighing in successive portions the mercury which it had held. The hydrogen from the voltameter was collected in this flask, without its stopper, the flask having been previously filled with mercury, with the needful precautions for removal of all air, and inverted over a mercury trough. In each experiment the process of electrolysis was arrested when the hydrogen had filled the body of the globe and reached to a point rather more than

half way down the length of the neck, the gold plates being of course withdrawn at the same moment from their cell of gold solution, set away to soak in distilled water, and afterwards thoroughly washed, dried, heated in the Sprengel vacuum, cooled, and weighed. The portion of hydrogen collected was dried by successive balls of fused potash introduced and withdrawn by means of platinum wire. The neck of the flask having, in advance of the collection of hydrogen, been passed through a cork, this was used to close the mouth, placed downwards, of a vessel through which a stream of water was caused to flow rapidly from the pipes supplying the University buildings. The atmospheric temperature of the day on which the electrolysis experiment was made having been such as not to differ too much from the temperature of the water from the pipes, the gas occupied such a volume after effectual exposure to this latter temperature that the mercury marked a point somewhere within the length of the neck, which point was noted by the millimeter scale, the thermometer immersed in the flowing water, and the barometer and its attached thermometer being read at the same time. It remained only to insert the stopcock stopper under the mercury of the little mercury trough, close the stopcock, withdraw the flask from the trough, reject the drop or two of mercury from the stopcock orifice by means of a wire, remove the portion of mercury left in the neck of the flask, and weigh it carefully. Its weight, with consideration of its temperature when the stopcock was closed, gave the volume of the portion of the flask not occupied by hydrogen, and, this, subtracted from the whole volume of the interior of the flask, as found by the original calibration, gave the volume, under known conditions of temperature and pressure, of the hydrogen which had been collected. From two calibrations at different temperatures a correction was obtained for the expansion of the glass of the flask, but it was hardly necessary to take this into account, in view of the small limits within which temperature varied in all the experiments made.

But three experiments carried out by this method led to results which seemed worthy of confidence. These results were as follows :

Experiment.	Character of gold in solution.	Character of gold in plates.	Gold deposited, grams.	Hydrogen liberated.	
				Vol. at 0° C. and 760 mm. cc.	Weight. gram.
I.	A, <i>b</i>	C	4.0472	228.64	.02053
II.	A, <i>b</i>	C	4.0226	227.03	.02039
III.	A, <i>b</i>	C	4.0955	231.55	.02079

In calculating the weight of hydrogen from its observed volume, Regnault's value for the weight of a liter of this gas at 0° C. and 760 mm. was taken as the basis. The correction, of which Lord Rayleigh not long since pointed out the need—namely, for the compression of the vacuous glass flask by atmospheric pressure—was adopted from the experiments of J. M. Crafts (*Comptes Rendus*, vol. 106, p. 1662); and his corrected value, .08988 gram, was still further corrected for the difference in the force of gravity at Paris and at the University of Virginia (in C. G. S. units, 980.94 : 979.95), giving as the value to be used .08979 gram.

The electrolysis of the water was carried on very slowly, so as to keep the density of the current low with such small electrodes as were used. Nevertheless, as the hydrogen voltameter required constant watching, it became necessary to bring the whole time of an experiment within moderate limits, and hence a considerably stronger current was used than in the simultaneous deposition of gold and silver in the fifth series, this circumstance being less favorable to the satisfactory deposition of the gold. It would have been desirable to use a larger flask and to collect a greater volume of hydrogen; but this, on account of the time required, would have made an experiment exceedingly troublesome and difficult.

In the work of this series the same unsatisfactory need for selecting only such results as came fairly close to the figures expected, and rejecting several others on the ground of very considerable departure therefrom, and the same sources of possible constant error in regard to the gold deposit, present themselves which have already been noticed under the head of the fifth series. As regards the hydrogen, one is led to consider possible diffusion of hydrogen and oxygen between the two little voltameter tubes, and slight imperfection in the drying of the hydrogen obtained. The former would, on the whole, probably tend to diminish the volume of gas collected, and hence to raise the apparent value of the atomic weight of gold. The latter would have the opposite tendency. That neither can have had more than an extremely minute influence was fairly proved by testing a part of the hydrogen obtained, on the one hand by passing it through a red-hot glass tube, and on the other hand by submitting it to more extended drying by contact with phosphorus pentoxide both before and after such heating; in neither case was there appreciable change of volume.

Notwithstanding the desirability of comparing the atomic weight of any other element directly with that of hydrogen, the difficulty is not to be overlooked of doing this for an element having so high an atomic weight as that of gold. There is a manifest objection to the necessity of dealing with such minute quantities of hydrogen as those concerned in these experiments. A very small error in the determination of the hydrogen greatly affects the value found for an atomic weight nearly two hundred times as large. It is true that the measurement of the volume of the hydrogen admits of being made with such precision as to leave room for but an extremely minute error in the corresponding weight, yet this measurement is not one of *limitless* delicacy, particularly if the difficulty be properly appreciated of ascertaining with certainty the precise temperature of the gas at the time its volume is read. Moreover, in measuring the volume of the gas, and thence deducing its weight, there is need not merely for a knowledge of changes of temperature and pressure, but for *absolutely* correct readings of the barometer and thermometer, so that there must usually be a degree of hesitation in accepting the readings of even fairly standard instruments, when temperature and pressure come to be placed in comparison with these conditions as affecting the results of Regnault for gaseous density. Nor can the results of that great physicist be assumed as themselves free from all possible need of further correction.

The error of direct comparison with so small an atomic weight as that of hydrogen is, however, after all only *masked* by substituting an *indirect* comparison through some larger atomic weight, since the assumed value of the latter is uncertain within limits which depend upon *its* comparison with the atomic weight of hydrogen.

Seventh Series of Experiments.

In pursuance of the attempt to connect directly the atomic weight of gold with that of hydrogen, metallic zinc was prepared as nearly as possible in a state of purity, and, a known quantity of the metal having been dissolved in dilute sulphuric acid, the amount of hydrogen evolved was determined by volume. A solution of pure auric chloride or bromide was then treated with a known quantity of the same zinc, more than sufficient for the complete precipitation of all the gold present; the excess of zinc

was dissolved by dilute sulphuric acid, and the volume of hydrogen given off was determined. The precipitated gold was carefully collected, washed, dried, ignited, and weighed. The difference between the volume of hydrogen which the zinc gave when thus partly used to replace a known quantity of gold and the volume which it would have given if replacing hydrogen alone represented, of course, the volume of a quantity of hydrogen equivalent to the gold precipitated and weighed. From this volume, under known conditions of temperature and pressure, the weight of the hydrogen was calculated on the basis of Regnault's results for the density of the gas, after application of the needful corrections, as in the sixth series of these experiments.

In a preliminary notice of my work read before the Chemical Section of the British Association at the Manchester meeting of 1887, it was pointed out that the method just described has certain advantages in principle. It does not require that the weight of the gold salt in solution be known, so that all difficulties in regard to drying such salt without decomposition are disposed of. It does not depend upon a knowledge of the atomic weight of the halogen in combination with gold, or upon a knowledge of the atomic weight of zinc. It does not even require that the zinc be of assured purity, provided only it be uniform in character, so that a given weight of it can be trusted to yield always the same quantity of hydrogen, and there be no impurities present capable of interfering with the collection of the whole of the precipitated metallic gold in a state of purity. The chief difficulty consists in the accurate ascertainment of the total volume of hydrogen evolved from the solution of a satisfactorily large quantity of zinc; when the gold solution comes to be used, as the volume of hydrogen given off on solution of the *surplus* zinc may be made quite small, its measurement becomes both easy and exact.

The pure zinc required was obtained by fractionally distilling in a Sprengel vacuum some very nearly pure metal from the Bertha Zinc Works, in Southwestern Virginia, using a long combustion-tube of hard Bohemian glass, and substantially the same arrangement of apparatus as that described by Morse and Burton¹ in connection with their work on the atomic weight of zinc. The original metal was found, by an analysis in the laboratory of the

¹ This Journal 10, 312. Tubes of glazed porcelain, closed at one end, had been specially procured for use in thus distilling zinc, but it was found that they were quite unnecessary.

University of Virginia, to contain less than .04 per cent. of foreign matter, almost solely consisting of lead and iron. It was four or five times redistilled *in vacuo*, rejecting each time about one-third of the quantity treated. The process is easily carried out, and in the final product, completely soluble in dilute sulphuric acid without visible residue, no trace of detectable impurity could be found.

For the evolution of hydrogen on solution of this zinc in acid the little piece of apparatus represented in Fig. 8 was used, the same that I had used in my work of several years ago on the atomic weight of aluminum.¹ The description formerly given of the details of an experiment with this apparatus may be repeated with but trifling change of language. A rather more than sufficient

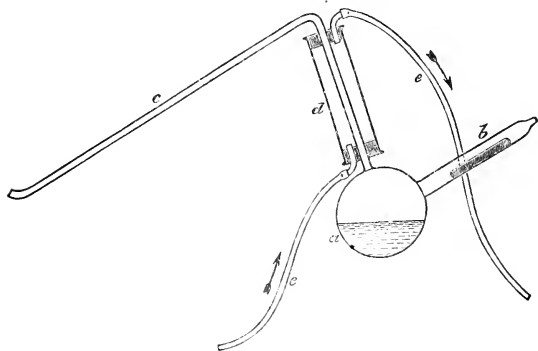


FIG. 8.

quantity of diluted sulphuric acid, its volume accurately measured, having been introduced into the bulb *a* by means of a little tube-funnel passed through the tube *b*, the outer end of which was originally open, taking care to leave the surface of *b* clean, the metallic zinc, in a single piece of elongated shape, and having a little bit of slender platinum wire wrapped round it, was passed into *b*, held nearly horizontal, so that the metal did not slip down into the bulb, but rested 40 or 50 mm. from it; *b* was now drawn off in the lamp flame, and sealed with a well-rounded end. The bulb was

¹ Phil. Trans. 1880, 1026.

touched for a moment or two with the hand, so as to expel a very little air, and the outer end of the small tube *c* was introduced into the mercury of the trough, taking care that *b* was still kept in such a position as to prevent the zinc coming in contact with the dilute acid. After a sufficient lapse of time for the apparatus to have acquired the temperature of the room, the barometer and thermometer and the difference of level of the mercury in the trough and in *c* were read off;¹ so that, knowing the volume of dilute acid introduced and of metallic zinc (the latter from its weight), calibration of the bulb and tubes after the experiment was over completed the data necessary to determine the volume of air which the apparatus contained at the beginning. The piece of zinc was now made to slide down into the bulb, the end of the gas delivery-tube *c* having been brought under the mouth of the measuring flask. Over-rapid evolution of hydrogen and any considerable rise of temperature were prevented, partly by tilting the bulb so that the little piece of zinc rested against one side and exposed but a part of its surface to the action of the liquid, and partly by cooling the outside of the bulb with water. To guard against more than traces of aqueous vapour being carried away with the hydrogen, a rapid current of ice-water was kept up through *d*.

As soon as the last of the zinc had disappeared, leaving the liquid quite clear, *c* was brought up into a nearly vertical position, and the apparatus left to itself until the temperature of the room had been attained. The barometer and thermometer and the height of the mercury in *c* above that in the trough were now read and recorded.

Lifting *c* straight up from the trough, the mercury in this tube was got out by running a wire up and down in it, and inverting it, the whole of the remaining space in *a*, *b*, and *c* was filled up with solution of zinc sulphate and free acid of the same strength with that already contained, this liquid being run in from a graduated burette through a slender tube-funnel, and the volume used noted, so as to show how much liquid had been already present.

The apparatus having been now emptied, washed out, and calibrated (with water, instead of mercury, on account of the difficulty of getting the interior quite dry), the volume of gas remaining in it at the close of the experiment was had from the difference

¹ All readings were, of course, made from a distance with the aid of a small telescope.

between the total capacity (to the level of the mercury in *c*) and the volume of liquid which the bulb had contained at the close of the experiment, these taken together with the data for pressure and temperature.

The dilute acid was saturated with pure hydrogen just before being used (and in the experiments with auric chloride or bromide the main portion of water holding this salt in solution was similarly treated), and a preliminary experiment showed that there was but an extremely minute difference between the amount of gas removable from such liquid by heating in a Sprengel vacuum and from that containing zinc sulphate after the solution of the metal; so that, practically, the question of retention of gas in solution by the liquid might be neglected.

The sulphuric acid was diluted to 25 per cent. by weight, only a small bit of platinum wire was wrapped round the zinc, and the temperature of the bulb was not allowed to rise beyond about 20° C. Thus the risk of evolving other gaseous products than hydrogen¹—as hydrogen sulphide or sulphur dioxide—was avoided, and on testing for these impurities the hydrogen collected no traces of them were found.

The measuring flask used to collect the hydrogen was of the same character as that used for the experiments of the sixth series, but of much larger size, holding about a liter. The quantity of zinc taken for each experiment was calculated to give a volume of gas which, under the conditions of temperature and pressure of the day, would bring the mercury to somewhere near the middle of the neck, and the gas, previously dried by balls of fused potash, was measured after the temperature had been rendered as nearly as possible fixed by the circulation round the outside of the flask of an active stream of water from the laboratory supply pipes. On account of slight rise of temperature during the solution of the metal, the volume of hydrogen left in the bulb and tubes was always less than that of the air in the same at the beginning; and, after reduction to normal temperature and pressure, the difference had to be subtracted from the gas collected in the flask.

In the experiments with auric chloride or bromide the quantity of hydrogen given off on solution of the *surplus* zinc was so small that it could be easily measured in a little glass tube, the same

¹ Muir and Adie, "On the Interaction of Zinc and Sulphuric Acid," Chem. Soc. Jour. 1888, p. 47.

method of double calibration with mercury being used as for the larger volumes. In these experiments the bulb used had a second side tube, *f*, as shown in Fig. 9, to hold the sulphuric acid, while *a*

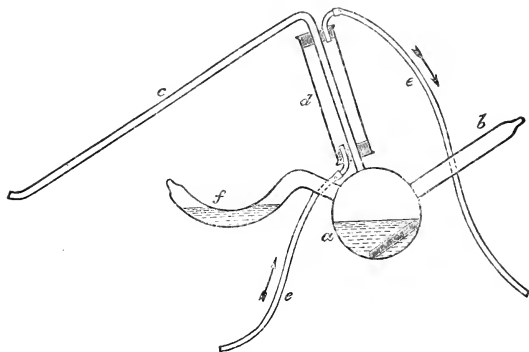


FIG. 9.

contained the aqueous solution of the gold salt; this acid was already somewhat diluted, and was introduced into *a*, after complete precipitation of the gold, very gradually, so as to avoid any considerable rise of temperature. The quantity of water used was such as to make the whole volume of liquid very nearly the same in the experiments with zinc alone and in those with zinc and the auric salt. Care was taken to ascertain, after measurement of the hydrogen, that it had been effectually freed by the potash balls not only from moisture, but from any traces of hydrochloric acid formed and carried over.

In order to connect the weight of the zinc with that of the hydrogen produced by its solution, it was necessary that the weight of the metal should be *absolute*, or in terms of equal value with those used in Regnault's researches on the density of hydrogen; hence, as has been already stated, the weights used were such as had had their real values determined, and the precaution of double weighing was applied. The quantities of metal used being small, the center of gravity of the balance beam was so adjusted as to give great sensitiveness. In calculating the weight of the hydrogen from its volume, the same value for the weight of a liter of the gas

was assumed as has been already stated, viz., .08979 gram, being the result of Regnault's determinations, with the correction pointed out by Lord Rayleigh and numerically estimated by Crafts, and further corrected for the force of gravity at the University of Virginia.

The haloid salts of gold were prepared as for the experiments of the first and second series, and the careful filtration of their solutions was followed by long continued standing at rest before the portions required were gently drawn off for use. Great care was taken in removing the last traces of precipitated gold from the bulb—to facilitate which the connected tubes were all cut off short—and in repeatedly washing the metal, first with dilute sulphuric acid, and then with pure hydrochloric acid, and, finally, with water, before drying, heating (in the Sprengel vacuum), cooling, and weighing.

The results obtained by this method were much freer from irregularity, and much more satisfactory, than those of the electrolytic experiments. All are reported, except one or two cases obviously vitiated by mechanical defects of manipulation, and, in consequence, not carried out to the end.

Experiments with Zinc alone.

Experiment.	Zinc dissolved. grams.	Hydrogen obtained at 0° C. and 760 mm. cc.		Hydrogen, at 0° C. and 760 mm. for 1 gram of zinc. cc.
I.	2.6990	922.64	} Equivalent to }	341.85
II.	2.6771	915.33		341.91
III.	2.7029	924.20		341.93
IV.	2.7117	927.51		342.04

Or a total amount of 10.7907 grams of zinc gave 3689.68 cc. of gas,¹ equivalent to 341.93 cc. of hydrogen for 1 gram of zinc. This value was adopted in calculating the fifth column of the following table.

¹ These figures represent an atomic weight for zinc = 65.142, taking the weight of a liter of hydrogen at 0° C. and 760 mm. as .08979 gram, and assuming the zinc used to have been absolutely pure, and the quantity of hydrogen collected to have been strictly equivalent to it; neither of the two latter assumptions is essential to the use made in this paper of the experiments. Reynolds and Ramsay in their recent paper (Chem. Soc. Jour., Dec. 1887, p. 854) on the atomic weight of zinc arrive at a somewhat higher value, on the basis of a like comparison of the weight of the metal with the volume of hydrogen liberated by it, but they assume the weight of the liter of hydrogen under normal temperature and pressure as .0896 gram, which must be considered too low in view of the recently applied correction of Lord Rayleigh.

Experiments with Gold Salt and Zinc.

Experiment.	Character of gold used.	Character of gold salt.	Gold precipitated, grams.	Hydrogen, at 0° C. and 760 mm.		Hydrogen equivalent to gold.	
				Corresponding to total zinc, cc.	Obtained from residual zinc, cc.	Vol. at 0° C. and 760 mm. cc.	Weight, gram.
I.	A, b	AuCl ₃	10.3512	1779.44	—23.34	=1756.10	=.15768
II.	A, b	AuBr ₃	8.2525	1428.99	—28.61	=1400.38	=.12574
III.	A, b	AuCl ₃	8.1004	1393.43	—18.56	=1374.87	=.12345
IV.	C	AuCl ₃	3.2913	582.82	—24.18	= 558.64	=.05016
V.	C	AuBr ₃	3.4835	606.20	—15.27	= 590.93	=.05306
VI.	D	AuBr ₃	3.6421	643.31	—25.20	= 618.11	=.05550

In considering possible causes of constant error in the experiments of this last series it seems most likely that they would affect the exact determination of the weight of the precipitated gold, either by mechanical loss of some minute particles of the metal, tending to lower the atomic weight, or by incomplete washing out of the zinc salt, with an influence in the opposite direction. Any failure to remove the last traces of moisture from the hydrogen was, I think, effectually guarded against, at any rate within such limits as would have sensibly affected the resulting atomic weight; and any error due to retention of hydrogen in solution by the liquid must also have been inappreciably small, in view of the precautions taken and the close similarity of conditions in the experiments with zinc alone and with zinc and the auric salt.

Calculation of Results.

In calculating the atomic weight of gold from the data furnished by the experiments which have been described, I have thought it best to conform to the most general usage of those who have been working on questions of this sort of late years, so as to facilitate comparisons with the results of others. Hence, although the atomic weight has been calculated separately from the figures of each experiment reported, the value deduced from each series has not been taken as the arithmetical mean of the separate results, nor has the probable error of these or of the mean been calculated by the method of least squares, as was done in my paper on the atomic weight of aluminum, but, instead, the general result for each series has been obtained, as in the calculations of Meyer and Seubert, from the aggregate quantities of the materials employed,

though I am by no means convinced that this mode of reckoning is in all cases sound in principle, giving, as it does, weight to each experiment in proportion to the quantity of material employed.

The atomic weight assumed for the other elements involved are those which have been most generally accepted in calculations of this kind, based for the most part on the experiments of Stas, and representing, with greatest probability, the values as at present known to us. They are as follows:

$$\begin{aligned} \text{H} &= 1. \\ \text{Ag} &= 107.66. \\ \text{Cl} &= 35.37. \\ \text{N} &= 14.01. \\ \text{C} &= 11.97. \end{aligned}$$

Calculated Results.

The following are the values obtained for the atomic weight of gold from the different series of experiments:

First Series ($\text{Ag}_3 : \text{Au} :: 322.98 : x$).

Experiment.	Silver, grams.	Gold, grams.	Atomic weight of gold.
I.	12.4875	7.6075	196.762
II.	13.8280	8.4212	196.694
III.	11.3973	6.9407	196.688 Lowest value
IV.	5.5286	3.3682	196.770 Highest value
V.	4.6371	2.8244	196.723
	<hr/>	<hr/>	<hr/>
	47.8785	29.1620	196.722

Second Series ($\text{Ag}_3 : \text{Au} :: 322.98 : x$).

Experiment.	Silver, grams.	Gold, grams.	Atomic weight of gold.
I.	13.5149	8.2345	196.789
II.	12.6251	7.6901	196.731 Lowest value
III.	17.2666	10.5233	196.843 Highest value
IV.	4.5141	2.7498	196.746
V.	5.8471	3.5620	196.756
VI.	6.4129	3.9081	196.828
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	60.1807	36.6678	196.790

Third Series ($\text{Ag} : \text{Au} :: 430.64 : x$).

Experiment.	Silver, grams.	Gold, grams.	Atomic weight of gold.
I.	12.4851	5.7048	196.772
II.	17.4193	7.9612	196.817 Highest value
III.	5.3513	2.4455	196.799
IV.	9.1153	4.1632	196.685 Lowest value
	<hr/>	<hr/>	
	44.3710	20.2747	196.775

Fourth Series ($\text{N}(\text{CH}_3)_3\text{HCl} : \text{Au} :: 201.40 : x$).

Experiment.	Loss by ignition of trimethyl-ammonium auri-chloride, grams.	Gold, grams.	Atomic weight of gold.
I.	7.5318	7.3754	197.218
II.	7.8432	7.6831	197.289 Highest value
III.	5.2811	5.1712	197.209
IV.	3.3309	3.2603	197.131 Lowest value
V.	2.8165	2.7579	197.210
	<hr/>	<hr/>	
	26.8035	26.2479	197.225

Fifth Series ($\text{Ag} : \text{Au} :: 107.66 : x$).

Experiment.	Silver, grams.	Gold, grams.	Atomic weight of gold.
I.	2.8849	5.2721	196.747
II.	3.4487	6.3088	196.945 Highest value
III.	2.3393	4.2770	196.837
IV.	1.9223	3.5123	196.709 Lowest value
V.	2.0132	3.6804	196.817
	<hr/>	<hr/>	
	12.6084	23.0506	196.823

Sixth Series ($\text{H} : \text{Au} :: 1 : x$).

Experiment.	Hydrogen, grams.	Gold, grams.	Atomic weight of gold.
I.	.02053	4.0472	197.136
II.	.02039	4.0226	197.283 Highest value
III.	.02079	4.0955	196.994 Lowest value
	<hr/>	<hr/>	
	.06171	12.1653	197.137

Seventh Series ($\text{H}_2 : \text{Au} :: 3 : x$).

Experiment.	Hydrogen, grams.	Gold, grams.	Atomic weight of gold.
I.	.15768	10.3512	196.941
II.	.12574	8.2525	196.894
III.	.12345	8.1004	196.851
IV.	.05016	3.2913	196.848 Lowest value
V.	.05306	3.4835	196.956 Highest value
VI.	.05550	3.6421	196.865
	<hr/>	<hr/>	
	.56559	37.1210	196.897

General Mean of Results.

If each of the foregoing series of experiments be represented by the result calculated from the aggregates of material used, and if equal weight be attached to the results of all the methods, the general mean derived from the whole of the 34 experiments will be as follows :

First series,	196.722	Lowest value
Second series,	196.790	
Third series,	196.775	
Fourth series,	197.225	Highest value
Fifth series,	196.823	
Sixth series,	197.137	
Seventh series,	196.897	
<hr/>		
General mean,	196.910	

The results of the fifth and sixth series, obtained by electrolysis, are, I am convinced, much less entitled to confidence than any of the others. If these two be excluded, the general mean of the remaining series will be 196.882, a number differing but little from the mean of all.

The highest value is that derived from the fourth series—ignition of trimethyl-ammonium auri-chloride. It has been seen that the individual results of this series agree fairly well with one another, and, when examined in connection with the facts as to the different crops of crystals of the salt used, do not seem to present any evidence of want of uniformity in the material. But, as it may still be suspected that traces of dimethyl- or of monomethyl-ammonium auri-chloride may have been present, and have caused the apparent value of the atomic weight of gold to come out higher than the truth, if we exclude also this series, the general mean of the remaining four will be 196.796.

Finally, if for the sake of comparison with the results of Krüss, and of Thorpe and Laurie, the general mean be taken for the first three series only, in which auric chloride and bromide were examined, the result is 196.762—intermediate between the general means of the two previous researches, but rather nearer to that derived from the work of Thorpe and Laurie than of Krüss.

It will be observed that, although there is pretty close agreement among the means of results obtained by altogether different

methods, this agreement is not so close as that presented by the results of the nearly similar methods pursued in the first three series. This cannot but suggest the probability of there being still sources of minute errors inherent in the methods themselves, and not dependent upon mere imperfections of manipulation in carrying these methods out. Although there is thus to be noticed a slight tendency on the part of each method to yield high or low figures severally, with the exception of the results of the fourth series there does not appear to be any considerable reason to see in the values obtained confirmation of the special suspicions in connection with each method which have been stated. There is no clear evidence of any difference in the results which can be traced to the history of the particular samples of gold used; a larger number of somewhat low results seem to have been yielded by the metal designated as (C)—*i. e.*, obtained from the United States Assay Office at New York—than by the others, but the difference is not marked or constant enough to warrant any trustworthy conclusions as to the character of this material.

Concluding Remarks.

The atomic weight of gold as deduced from the experiments reported in this paper is entirely in accord with the place occupied by the metal in Mendelejeff's "periodic" classification of the elements, but this is equally true of the slightly different values obtained by Krüss, and by Thorpe and Laurie, and the only difficulty at one time apparent as to this point—namely, the relative positions of gold on the one hand and of platinum, iridium, and osmium on the other—has been removed, not by any change in the atomic weight of gold, but by changes affecting the values to be assigned the three other metals, as these values have been determined by Seubert.¹ It is very desirable that, in order to a fuller and more exact examination of the Mendelejeff table of the elements, there be accomplished as soon as possible a general revision of the atomic weights of *all* the elements of well determined individuality, so many of which are still very imperfectly known.

As to any bearing of the results of the present paper on the

¹ Ber. d. chem. Ges. **11**, 1770; **14**, 868; **21**, 1839.

so-called hypothesis of Prout,¹ the general mean of all my results, or even the general mean with exclusion of the values obtained by electrolysis, approaches the integer number 197 rather more nearly than does the final number arrived at by Thorpe and Laurie, and still more nearly than does that considered by Krüss to express the final result of his experiments. If the results of the fourth series be also rejected, my general mean will be nearer the integer than is the Krüss number, but not quite so near as that of Thorpe and Laurie. I feel that somewhat greater confidence may be placed in my own work, simply on the ground of its involving the use of more completely different and independent methods—a principle which I believe to be of the first importance in any attempts at increased accuracy in the determination of atomic weights.

At the same time, as has already been pointed out, this work seems to me to furnish some probable evidence that not all inherent defects of method have been eliminated. Whether or not such defects may exist to an extent sufficient to account for the remaining difference between the value obtained and the integer multiple of the atomic weight of hydrogen there does not seem to be ground on which to express a positive opinion. But this research does not supply any clear evidence contradictory of such a possibility.

On this point, and generally on the attainment of what is sometimes rather too easily spoken of as the greatest possible accuracy in the determination of an atomic weight—particularly of an element for which the value is as high as that for gold—any one who actually works in a conscientious way at such determinations will be pretty sure to feel more strongly the difficulty of the task, and to express himself with more caution, than do some compilers of results in assuming at any time that the last word has been spoken.

¹ Soon after the publication of my paper on the atomic weight of aluminum, I was criticised by a writer of abstracts for the German Chemical Society on account of my use of the expression "Prout's law," amazement being indicated that I should have called the "hypothesis" of Prout a law. If this writer had noticed my use of inverted commas, and still more what was said in the course of two or three pages of the paper, he would have seen that the use of the expression "Prout's law" was by no means equivalent to assuming this to be "a law of nature."

THE ELECTROLYTIC METHOD AS APPLIED TO
PALLADIUM.

BY EDGAR F. SMITH AND HARRY F. KELLER.

Our knowledge bearing upon the behavior of this metal towards the current is limited and rather indefinite. In 1868 Wöhler published, in the *Annalen*, 143, 375, an article entitled "Ueber das Verhalten einiger Metalle im elektrischen Strom," from which the following facts are taken: palladium, as the positive pole of a battery consisting of two Bunsen cells, was immersed in water acidulated with sulphuric acid, when the metal immediately became coated with a deposit having a bright steel-like color. This deposit is doubtless palladium dioxide, as it liberates chlorine when treated with hydrochloric acid, and carbon dioxide when warmed with oxalic acid. At the same time black, amorphous metal separated upon the negative pole. Its quantity was slight. In the second edition of Classen's *Quantitative Electrolysis*, p. 72 (Am. edition), it is stated that a feeble current will deposit palladium in a beautiful metallic state from an acid solution. One Bunsen cell is given as sufficient for this purpose. A more energetic current produces a spongy deposit. Ludwig Schucht has communicated¹ that from an aqueous solution of palladious nitrate, acidulated with a few drops of nitric acid, the current precipitated upon the negative pole a bronze-colored deposit, which, as it grew more dense, became darker, and finally black in color. At the positive pole there was a simultaneous deposition of oxide, showing a reddish color. In alkaline palladic solutions the precipitation of metal was much retarded; the deposition of oxide was also observed.

Our first experience in the electrolysis of palladium salts was acquired from the double cyanide in an excess of potassium cyanide. In such solution a current, generating 1 cc. oxyhydrogen gas per minute, failed to cause metallic deposition until after the expiration of thirty-six hours; in other words, not until the excess of potassium cyanide had been completely converted into alkaline carbonates. Then the deposit was black in color, but the precipitation was not at all complete. No deposition of oxide was noticed upon the positive pole. The conduct of the metal in cyanide

¹ *Berg- und Huttenmännische Zeitung* 38, 121; also *Zeit. für anal. Chem.* 22, 240.

solution led to the trial of certain separations, the results of which will be given in a later communication. The action of the current (feeble) was also tried upon a solution of palladious chloride, in the presence of a large excess of potassium sulphocyanide. In this case the deposition of metal was exceedingly rapid. Spongy spots were noticeable. The deposit was black in color. The experiment was made with this solution in the hope that possibly a separation of copper from palladium might be found; but as these metals separate with equal rapidity from their sulphocyanides, the results are valueless for this purpose.

The next attempt was made with palladammonium chloride, $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$, in just sufficient ammonium hydroxide to retain it in solution. The total dilution of the solution was 125 cc.; the acting current gave 0.9 cc. OH gas per minute. The poles were distant from each other about two inches. Just as soon as the circuit was completed, a yellowish brown coating appeared upon the spiral of the positive pole; while upon the dish, in connection with the negative pole, a deposit of metal closely resembling the platinum itself in color made its appearance. After acting through the night the current was interrupted, the metal deposit carefully dried and weighed. The precipitation was incomplete. It was, however, discovered that the deposition at the positive pole, which gradually increased in mass and assumed a black color, had entirely disappeared. In all instances where the ammonium hydroxide was in decided excess, the precipitation of oxide on the positive pole was not observed. This behavior is similar to that of nickel when its ammoniacal solutions are electrolysed. In subsequent experiments the course was somewhat modified. From solutions such as just described, the palladium thrown out upon the platinum dish was extremely slow in dissolving, even in fuming nitric acid, so that it was deemed expedient to first coat the platinum dishes employed in the electrolysis with a layer of silver, varying in weight from 0.1–0.3 gram. This was done in the experiments recorded below, and was found to be decidedly advantageous. The layer of silver seemed to hasten the deposition of the palladium.

Experiment I.—A quantity of palladammonium chloride (\equiv 0.2228 gram Pd) was dissolved in ammonium hydroxide; to this solution were added 20–30 cc. of the same reagent (sp. gr. 0.935) and 75 cc. water. The current allowed to act upon this ammoniacal liquid gave 0.9 cc. oxyhydrogen gas per minute. The

It may be remarked that in filling the silvered platinum dishes a rather large surface of silver was allowed to remain above the electrolysed liquid, so that by merely adding water it was possible to ascertain when the palladium was fully precipitated. When the deposition was not finished the new silver surface soon showed streaks of metal.

A third series of two experiments, in which the added amount of palladium was double that recorded in the preceding examples, the same conditions were observed as before, with the exception that as the current was only giving 0.70 cc. oxyhydrogen gas per minute, the time of precipitation was extended to eighteen hours. The results were as follows :

$$\begin{array}{rcl} \text{Experiment V.} & \text{Weight of silvered dish + Pd} & = 72.3555 \\ & \text{“ “ “ “ — Pd} & = 71.9100 \\ & \text{Weight Pd} & = 0.4455 \end{array}$$

$$\begin{array}{rcl} \text{Experiment VI.} & \text{Weight of silvered dish + Pd} & = 62.2600 \\ & \text{“ “ “ “ — Pd} & = 61.8138 \\ & \text{Weight Pd} & = 0.4462 \end{array}$$

Curiously enough, upon warming the liquid poured off from the palladium in Experiment V, with ammonium sulphide there appeared a very slight sulphide precipitate after some hours. The liquid from Experiment VI showed no trace of unprecipitated metal.

The deposits in the experiments just recorded were bright, metallic and very dense. In none was there the slightest tendency to sponginess. To show the accuracy of the method the results may be tabulated as follows :

	Found Pd.	Calculated Pd.
Experiment I.	0.2225	0.2228
“ II.	0.2225	“
“ III.	0.2230	“
“ IV.	0.2232	“
“ V.	0.4455	0.4456
“ VI.	0.4462	“

If the percentage differences be calculated it will be found that they are quite within the limit of error occurring in almost any ordinary gravimetric determination.

The behavior of ammoniacal palladium solutions, when exposed to the action of the electric current, will be further studied as time permits, and, if possible, the attempt will be made to re-determine the atomic weight of the metal by this method in a somewhat modified form.

UNIVERSITY OF PENNSYLVANIA, *February 12, 1890.*

Contributions from the Chemical Laboratory of the Department of Agriculture.

XV.—ORGANIC ACIDS IN THE JUICES OF THE SORGHUM CANE.

BY H. W. WILEY AND W. MAXWELL.

Preliminary investigations with the juices of the sorghum cane have indicated the presence of the following acids, which have been obtained as free crystallised bodies, or as salts :

A. Volatile	{	1. Formic acid.	
		2. Acetic "	
B. Oleics	{	3. Prismatic crystals.	} Undetermined.
		4. Needle "	
		5. Oxalic acid.	
		6. Tartaric "	
C. Other acids	{	7. Citric "	
		8. Malic "	
		9. Aconitic ¹ "	

These preliminary examinations indicate that the given acids are present in the following order by proportion :

Aconitic, citric, malic, oleic, formic, with decreasing amounts of the others, terminating with mere traces of oxalic and acetic acids.

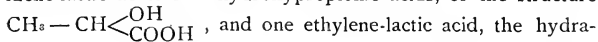
For want of material the researches will stand over until next season for completion.

¹ See Parsons, this Journal 4, on Aconitic Acid in Sorghum.

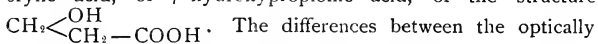
NOTES.

Ethylene-lactic Acid.

In the work of Wislicenus in 1868 and that of Erlenmeyer in 1875, the existence of three lactic acids was definitely proved, and their properties and modes of formation studied. Two ethylidene-lactic acids or α -hydroxypropionic acids, of the structure



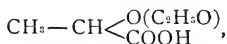
crylic acid, or β -hydroxypropionic acid, of the structure



inactive ethylidene-lactic acid and the optically active modification—sarcosolactic acid—are those we should expect if we accept the hypothesis of Van't Hoff and Le Bel, of physical isomerism due to the presence of an asymmetric carbon atom. Our received theories then account for the existence of these three lactic acids and no more; but Wislicenus isolated from the mother-liquors of zinc sarcosylactate a zinc salt, which he supposed to be the salt of an ethylene-lactic acid; he proved that it was not a salt of hydrocrylic acid. He could not isolate the ethylene-lactic acid, nor indeed force the syrupy zinc salt to crystallise, but he made and analysed a sodium salt. Mention of this fourth supposed lactic acid found its way into the text-books, and until now this has been one of the doubtful points in chemistry.

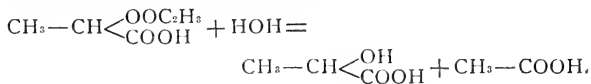
Max Siegfried, of the Physiological Institute in Leipsic, publishes a paper in No. 14, Vol. 22, of the *Berichte der deutschen chemischen Gesellschaft* for 1889 which satisfactorily explains the formation and reactions of this zinc salt.

By extracting with alcohol the mother-liquors of the zinc sarcosylactate from one hundred pounds of horse-flesh, the author obtained a syrupy zinc salt having the properties described by Wislicenus; it was not found possible to crystallise the zinc or calcium salt, but crystallised sodium and silver salts were obtained and analysed. The percentage of sodium and of silver was not that of lactates, but by substituting the value of hydrogen for that of silver, in the figures, the formula $(\text{CH}_2\text{O})_n$ results. It was observed that the zinc salt when precipitated by ether from its alcoholic solution was not completely soluble in water; Siegfried thought it possible to obtain the free acid from this insoluble portion, and after some difficulty he succeeded in isolating from it an acid crystallising in needles, and fusing at 166° – 167° , which he analysed and found to be acetyl-lactic acid,



identical with an acetyl-lactic acid made by Wislicenus from a derivative of inactive ethylidene-lactic acid. The author shows

that this acid and its salts are unstable and break down readily in presence of water into acetic and lactic acids,



This behavior explains the figures obtained in the analyses of the salts. Wislicenus found 24.2 per cent. sodium in his sodium salt, and this is the exact figure demanded for a mixture of equal parts of sodium acetate and lactate. The author's figures for sodium varied from 25.74 to 25.81; values lying between those for sodium lactate and acetate. The author's analysis of the silver salt led to the assumption of an acid $(\text{CH}_2\text{O})_n$, a formula common to both acetic and lactic acids.

But why should zinc acetyl-lactate be stable when the sodium and silver salts are so readily decomposed? The answer lies in the curious fact that by the action of zinc acetate on zinc sarcolactate in aqueous solution, zinc acetyl-lactate is invariably formed, and the presence of very little of this substance prevents zinc lactate and zinc acetate from crystallising. The zinc salt found by Wislicenus then was zinc acetyl-lactate, not zinc lactate, and with this falls all evidence of the existence of a fourth lactic acid.

In the liquids extracted from meat acetic acid is always present, hence the formation of the zinc acetyl-lactate is clear.

The author has made the acetyl-lactic acid synthetically from zinc lactate and zinc acetate. Solutions of acetyl-lactic acid and of its zinc salt are optically inactive, and on saponification of the acetyl-lactic acid, a salt of inactive ethylidene-lactic acid is formed. On taking up the acetyl group, then, the ethylidene-lactic acid changes from the active to the inactive modification. It may be inferred, then, that inactive ethylidene-lactic acid could be substituted for the active modification in the synthesis of acetyl-lactic acid, and Siegfried finds this to be the case; the products in both instances are identical.

E. R.

UNITED STATES DEPARTMENT OF AGRICULTURE,
DIVISION OF CHEMISTRY,
WASHINGTON, D. C., Feb. 6, 1890.

Editor CHEMICAL JOURNAL:

I beg the favor of calling attention to the fact that the formula given for calycanthine on page 566 of No. 8, Vol. XI, AMERICAN CHEMICAL JOURNAL, is incorrect. The analytical data were sent to me at Toronto last year during the meeting of the American Association, and a mistake of a 7 for a 4 is the cause of the error.

An extensive study of this body with some associated alkaloids is now going on and the full data of the work will be sent to you in due time.

H. W. WILEY.

AMERICAN CHEMICAL JOURNAL.

THE ATOMIC WEIGHT OF MAGNESIUM AS DETERMINED BY THE COMPOSITION OF ITS OXIDE.

BY W. M. BURTON AND L. D. VORCE.

The method employed by Dr. H. N. Morse¹ and one of us (B) for the preparation of pure zinc and the determination of its atomic weight yielded such satisfactory results that it seemed desirable to employ the same process for the purification of other metals and for the redetermination of their atomic weights. Among others, magnesium was suggested as being suitable for the purpose because, like zinc, it can be distilled at a comparatively low temperature, and its nitrate, upon ignition, yields an oxide of definite composition, and stable when heated to a very high temperature.

Therefore, in accordance with an understanding with Dr. Morse, we have undertaken the redetermination of its atomic weight. Several investigators have determined the atomic weight of magnesium, but in almost every instance either some impurity was found to exist in the materials used, or else some defect was discovered in the method employed, thereby creating doubt as to the accuracy of the results obtained. The following methods have been used:

1. Composition of sulphate by action of sulphuric acid on the oxide (Berzelius,² Bahr,³ Svanberg and Nordenfeldt,⁴ and Magnac⁵).

¹ This Journal 10, 311.

² Pogg. Ann. 8, 188.

³ Jour. f. pr. Ch. 56, 310.

⁴ Ibid. 45, 474.

⁵ Ann. ch. phys. (6) 1, 321.

2. Determination of sulphuric acid in the sulphate by precipitation as barium sulphate (Scheerer,¹ Jacquelain,² and Gay-Lussac³).
3. Conversion of oxalate into oxide by ignition (Svanberg and Nordenfeldt⁴).
4. Conversion of sulphate into oxide by ignition (Gay-Lussac⁵).
5. Determination of chlorine in magnesium chloride (Dumas⁶).
6. Conversion of carbonate into oxide by ignition (Marchand and Scheerer⁷).

The results of these investigations are shown in the following table:

Date.	Investigators.	At. wt. Mg (O=16).	At. wt. Mg (O=15.95).
1819	Gay-Lussac	22.89	22.812
1820	"	24.18	24.102
1826	Berzelius	25.20	25.122
1846	Scheerer	24.11	24.032
1847	{ Svanberg Nordenfeldt	24.63	24.562
1850	Jacquelain	24.11	24.032
1850	{ Marchand Scheerer	23.96	23.882
1852	Bahr	24.74	24.662
1859	Dumas	24.48	24.502
1884	Marignac	24.38	24.302

The method which we propose is essentially the same as that which was used in the determination of the atomic weight of zinc, and previously described in this Journal.⁸ Slight changes have been made in some details of the manipulation, and these will be noted in their appropriate places. The magnesium was purified by distillation in a vacuum. Weighed portions of the metal were converted into the nitrate, which was ignited to the oxide, first in a hot-air bath, and finally at the highest temperature obtainable in a muffle furnace. The simplicity and directness of the method are strong points in its favor, and we believe we have eliminated the two general difficulties by which the accurate determination of the atomic weight of magnesium has been beset, viz. first, presence of impurities in the materials used; second, the error involved in determining these impurities and correcting for them.

¹ Pogg. Ann. **69**, 535.

² Ann. ch. phys. (3) **32**, 202.

³ Ibid. (2) **13**, 308.

⁴ Jour. f. pr. Ch. **45**, 474.

⁵ Loc. cit.

⁶ Ann. ch. phys. (3) **55**, 189.

⁷ Jour. f. pr. Ch. **50**, 385.

⁸ Loc. cit.

I. The Preparation of Pure Magnesium.

When an attempt was made to distill the magnesium in ordinary hard glass tubes, it was found that the vapors of the metal attacked the glass, forming a black voluminous substance which evolved a spontaneously inflammable gas when treated with an acid. The action of magnesium powder on silica and other oxides has been studied by Gattermann,¹ and his results lead us to conclude that the black substance which we obtained was magnesium silicide of the formula Mg_2Si , and the explosive gas was undoubtedly silicon tetrahydride. Further, when the silicide was dissolved in acid there remained a yellow substance which probably was the suboxide of silicon described by Mabery.² Repeated fractional distillation did not entirely separate this silicide of magnesium from the pure metal. In consideration of the fact that magnesium forms no alloys with iron, the idea suggested itself of using an iron tube inside the glass tube. Fig. 1 represents the

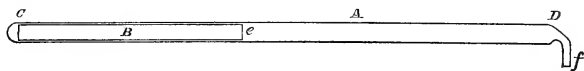


FIG. 1.

method of arrangement. *A* is a tube of hardest potassa glass, fused together at one end. *B* is tube made of thin sheet iron of the best quality obtainable. The iron tube was pushed into the glass tube as represented and then filled with small pieces of magnesium ribbon. The end of the iron tube at *e* is bent over in such a way as to prevent the carrying over of small pieces of magnesium during the distillation. About ten grams of the metal were used in each charge. The glass tube was connected at *f* with a Sprengel air-pump and the apparatus thoroughly exhausted. The tube was heated in a combustion furnace throughout its whole length, but most strongly at *B*. When the iron tube showed a bright red heat the magnesium commenced to volatilise and sublime on the cooler portions of the tube at *A*, forming at first a black mirror of magnesium silicide.

Our first plan was to use an iron tube extending from *C* to *D*, so that the glass would be entirely protected from the vapors of magnesium, but numerous experiments showed that the first

¹ Ber. d. chem. Ges. 22, 136.² This Journal 9, 14.

coating at *A* entirely protected the glass, so that subsequent portions of the metal were deposited without being contaminated with the silicide. Experiment also showed that the iron tube served to support the walls of the glass tube, as the latter would otherwise collapse when heated to the fusing point of magnesium. The tube at *B* was maintained at a bright red heat for about an hour, the gas was then turned down and the apparatus cooled very slowly. By taking proper precautions the cracking of the tube was prevented during the cooling process, thereby maintaining a vacuum in the apparatus until the end of the distillation. The portion of the metal remaining in *B* and that which had collected at *D* were rejected. The portion collected at *A* was three times redistilled; the magnesium which collected at *A* during the fourth distillation was employed for the atomic weight determination. It was deposited as a thin crystalline bar of pure white metal, which readily separated from the coating of magnesium silicide on the glass. In a few instances beautiful crystals of the metal were formed; these will be considered later in this paper. The magnesium deposited in the fourth distillation was carefully analysed, special pains being used in the tests for silicon, carbon, calcium and iron, but we were unable to detect any impurity whatever. It was also spectroscopically examined, but the spectrum showed no lines of impurities, the characteristic green lines of magnesium being the only ones visible. We analysed the magnesium ribbon used in the distillation and found small quantities of silicon, iron and carbon.

II. *Preparation of Pure Dilute Nitric Acid.*

Pure strong nitric acid was prepared by the method already described in this Journal.¹ In order that the magnesium might dissolve slowly, the nitric acid was diluted with an equal volume of water. The water was purified by distilling it first from acid permanganate of potassium, then from alkaline permanganate, and finally in the platinum apparatus which was used in preparing the nitric acid. The dilute acid was preserved in a platinum dish under a bell-jar, and a platinum spoon was used for transferring it as it was needed.

III. *The Method of Procedure.*

The conversion of the magnesium into its oxide was effected in porcelain crucibles, the arrangement of the crucibles being the same as that described in the article on the atomic weight of zinc. A piece of magnesium weighing about 300 milligrams was carefully broken off, and any clinging portions of dust removed by filing. A powerful lens was used in examining the metal, and it was not handled except by means of clean forceps. Having balanced a pair of crucibles with their appropriate tares, the difference in weight was noted. The piece of magnesium was then weighed into one of them and treated with dilute nitric acid. When the metal had disappeared, the excess of acid and water was evaporated, and the nitrate of magnesium partially decomposed by heating in a sand-bath. Finally the crucibles were placed in a muffle furnace and kept at a white heat for about two hours. After weighing, the oxide was again heated in the muffle, and as a rule one ignition was sufficient to insure constant weight. In some of the determinations, however, two ignitions were necessary. The tares were treated with dilute nitric acid, and heated in every instance like the crucibles in which the determinations were made. The magnesium oxide was tested for oxides of nitrogen by the method described by Griess.¹ The magnesium oxide was dissolved in dilute sulphuric acid, and two cubic centimeters each of sulphanilic acid and naphthylamine hydrochlorate were added. Not a trace of the pink color appeared. In another sample of the oxide, which was not ignited to constant weight, the iodide of starch reaction for testing for nitrous acid failed to give a blue color, while the sulphanilic acid test showed a distinct pink color.

IV. *The Weighing.*

The balance used was made by Becker Bros.; its capacity was one hundred grams, and it was sensitive to $\frac{1}{20}$ milligram with its full load. The balance case was inclosed in a tight-fitting wooden box, furnished with appropriate doors, through which the weights and crucibles could be transferred. All observations were made with these doors closed. A gas lamp and mirror were so arranged that the ivory scale of the balance could be illuminated through a small aperture in the box; the excursions of the pointer were

¹ Ber. d. chem. Gesell. 12, 426.

noted through a similar aperture situated just above the first. The methods of weighing by vibrations and of double weighing—that is, upon both pans—were employed throughout. The sensibility of the balance, with the load furnished by the crucibles, was determined at least once during each series of observations. Each weighing was made as rapidly as possible, allowing due time for noting observations accurately, as it is believed that an undue amount of time spent in weighing only increases the error due to changes in temperature and atmospheric conditions. Only the smaller platinum weights were used, since the magnesium oxide obtained in one experiment never weighed more than seven hundred milligrams. All weighings were made at night after the laboratory and streets in the vicinity had become quiet.

V. *The Results.*

The following table shows the result of ten successive experiments :

	Wt. of Mg.	Wt. of MgO.	At. wt. Mg (O = 16).	At. wt. Mg (O = 15.95). ¹
1	.33009	.54766	24.278	24.202
2	.34512	.57252	24.283	24.207
3	.26058	.43221	24.292	24.216
4	.28600	.47432	24.299	24.223
5	.30917	.51273	24.301	24.225
6	.27636	.45853	24.271	24.195
7	.36457	.60475	24.286	24.210
8	.32411	.53746	24.304	24.228
9	.32108	.53263	24.284	24.208
10	.28323	.46988	24.279	24.203
		Mean	24.287	24.211
		Highest	24.304	24.228
		Lowest	24.271	24.195
		Difference	.033	.033

If we calculate the atomic weight from the sums of the quantities of magnesium taken and oxide obtained as recommended by Meyer and Seubert,² we have :

Wt. of Mg.	Wt. of MgO.	At. wt. Mg (O = 16).	At. wt. Mg (O = 15.95).
3.10031	5.14269	24.287	24.211

¹ Value found by Keiser, this Journal 10, 249.

² Die Atomgewichte der Elemente, p. 13.

VI. Crystals of Magnesium.

Of the crystal form of magnesium very little is definitely known. The element is usually regarded as holohedral, hexagonal, and isomorphous with zinc and beryllium. The production of very perfect crystals during the distillation of our magnesium seemed of sufficient interest to warrant their study and description. Dr. G. H. Williams of the Johns Hopkins University undertook this work and kindly sent us his results for publication. The first account of magnesium crystals was given by Dumas¹ in 1880, who obtained them while experimenting with the gases absorbed by magnesium during distillation. Des Cloizeaux² measured these crystals and described them as hexagonal prisms with the unit pyramid and terminated by the basal plane. He obtained the axial ratio $a:c = 1:1.6391$.

The crystals which we obtained were about one millimeter in diameter, having very perfect planes which furnished, in most instances, sharp and distinct reflections on the goniometer. No planes appeared except OP, P and ∞P . The following table shows the angles measured on four different crystals with a large Fuess goniometer. In each crystal one or more zones of 180° were observed; when more than one zone was measured the mean result is stated and the number of zones upon which this average is based is given in parenthesis.

Crystal.	OP:P.	P: ∞P .	∞P :P'.	P':OP'
I	$61^\circ 47' (2)$	$28^\circ 12' (2)$	$28^\circ 17'$	$61^\circ 50'$
II	$61^\circ 44'$	$28^\circ 15'$	$28^\circ 00'$...
III	$61^\circ 55'$	$28^\circ 5'$	$28^\circ 3'$	$61^\circ 57'$
IV	$61^\circ 57' (3)$	$28^\circ 5' (3)$	$28^\circ 7' (3)$	$61^\circ 52' (3)$

The average of the twelve measurements of the angle OP:P is $61^\circ 52' 30''$; whose supplement is $118^\circ 7' 30''$. If we use this value for the axial ratio we have $a:c = 1:1.6202$, which is almost identical with the value obtained by Des Cloizeaux. It appears from these figures that magnesium is more closely related to beryllium, in its crystal form, than to zinc, as will be seen in the following statement:

Beryllium, $a:c = 1:1.5802$ Brögger.

Zinc, $a:c = 1:1.35642$ Williams and Burton (Am. Ch. Jour. **11**, 219).

Magnesium, $a:c = 1:1.6202$ Wilson.

¹ Comptes rendus **90**, 1027.

² Ibid. **90**, 1101.

Experiments were made to test the cohesive properties and slipping planes of the magnesium, but no results were obtained like those described in the investigation of zinc crystals.

It is with pleasure that we acknowledge our indebtedness to Professor Morley and Professor Mabery, who placed their laboratories at our disposal during this investigation. With such adequate facilities we were enabled to work much more rapidly and satisfactorily than we otherwise could have done.

CLEVELAND, O., *February, 1890.*

A MODIFICATION OF THE METHOD OF COMBUSTION WITH LEAD CHROMATE.

BY RUDOLF DE ROODE.

A modified method of combustion with lead chromate, which I have used with good results, is as follows: A mixture of about 4 parts by weight of finely divided lead chromate and 1 part by weight of red lead, after thorough washing, is sucked into a compact mass on a funnel with a pump. While still moist, the mass is divided with a spatula into lumps about the size of a pea. These lumps are heated to redness in small portions in a porcelain crucible. While hot they are of a dark brown or black color, but on cooling in the air the color changes to a bright red. The lumps are broken up in a mortar to about the size of grains of wheat. The larger grains are separated by a sieve from the smaller particles, which are pulverised and used for mixing with the substance to be analysed.

Into a combustion tube of a suitable length for the furnace is placed an asbestos plug (*A*), in front of which a piece of reduced copper gauze is to be put. From recent experiments it has been shown that the presence of this copper is necessary, whether the substance to be analysed contains nitrogen or not. The tube is then filled to about two-thirds of its length with the coarse grains of the preparation, which are held in place by a second asbestos plug (*B*). Behind this plug is introduced the substance to be analysed, mixed with some of the finely powdered preparation. The mixing is best accomplished as follows:

The tube is held in a vertical position with the front end down. On top of the asbestos plug (*B*) a layer of the finely powdered preparation about two inches thick is introduced by means of a small copper funnel. The weighed substance, on a small watch-glass, is then introduced through the funnel, and the glass, funnel, and walls of the tube rinsed with small portions of the finely powdered preparation until a second layer of about two inches in thickness has been added (to *E*). The substance (which is now at *C*) is mixed intimately with the fine powder (from *B* to *E*), either by means of a clean copper wire, or better, by closing the end of the tube and shaking and turning it about in the tube. The remainder of the tube (to *F*) is then filled with the coarsely granular preparation. A channel is made for the free passage of the gases along the entire length of the tube by striking it longitudinally on a flat surface. The tube is placed in the furnace, connected in front with the calcium chloride tube, potash bulbs, etc., and behind with an apparatus furnishing pure dry air. The clamp (at *G*) is closed tight and the tube heated in front (nearly up to *B*) to a bright red heat. The gas-jets are then turned on from behind (at *F*), and the combustion conducted as usual. When the combustion is completed the apparatus is connected with an aspirator, which is set in operation and pure dry air admitted by opening gradually the clamp (*G*), by which clamp the current of air may be regulated. The tube is kept hot, especially at the portion (*BE*) where the substance was contained, for about 10 or 15 minutes while the current of air is being drawn through. The tube is then allowed to cool slowly while about a liter of air is drawn through. The weighed bulbs and tubes are then disconnected, the tube closed tightly in front, and left in connection with the dry air behind until cool. If not broken, the tube may be used over and over without disturbing the portion between *A* and *B*. The stopper is taken out behind and the coarse grains (from *F* to *E*) removed. The portion (from *E* to *B*) which contained the substance is scraped out and discarded. The tube is then filled



as before for another combustion, a fresh piece of reduced copper gauze being put in front, if necessary.

This granulated mixture of lead chromate and oxide does not fuse at a red heat, thus rendering it preferable to pure, fused lead chromate. In the granulated form it presents a larger surface of action than powdered lead chromate, and thus possesses all of the advantages of copper oxide.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

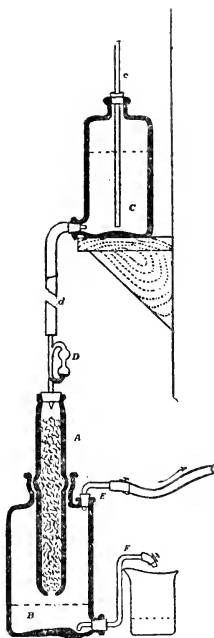
A SELF-REGULATING GAS-GENERATOR ON A NEW PRINCIPLE.

BY H. W. HILLYER.

The accompanying diagram illustrates a form of gas-generator devised by the writer especially to supply hydrogen sulphide for this laboratory. But as the apparatus seems to have several points of advantage over those now in use, in cases where large quantities of gas are to be generated; where a considerable pressure is required; and where the apparatus does not often need to be moved, it may be found useful in other places if made known by this notice.

The apparatus consists of two principal parts, the acid reservoir (*C*) and the generator (*AB*). The acid reservoir is a common aspirating bottle of a gallon or more capacity, provided with a stopper and glass tube (*c*) to regulate the liquid pressure, on the principle of the Mariotte bottle. A piece of stout rubber tubing (*d*) connects it with a bulb tube (*D*) drawn out at its lower end to an opening of about one-sixteenth of an inch in diameter and passing through the rubber stopper in the cylinder (*A*). The generator consists of the glass cylinder (*A*) and the outer glass vessel (*B*) which are ground or cemented together gas-tight. The cylinder (*A*), about two and a half inches in diameter and twenty inches in length, serves to hold the ferrous sulphide, zinc or marble over which the acid trickles or rather is forced by the gas generated. The vessel (*B*), about nine inches in diameter and eighteen in height, serves two purposes, first as a reservoir for waste acid, secondly, as a reservoir in which is stored gas generated and not immediately needed.

The acid flows from (C) through (d) and (D) into (A). The gas generated, finding no outlet at the top of the cylinder, forces the acid over the contents of the cylinder into (B) and escapes through (E). When a less rapid evolution of gas is required, its flow through (E) is checked, the pressure inside the generator soon becomes great enough to balance the column of acid, which stops flowing so rapidly, and the generation of gas is diminished or ceases entirely if (E) is fully closed. A too sudden and excessive accumulation of pressure, which might force the acid out of (Dd) back into (C) or drive out the stoppers, is prevented by having the vessel (B) of large capacity. If (E) is closed suddenly, even when the apparatus has been working quite rapidly and a considerable quantity of acid is still acting on the solid reagent, the capacious vessel gives room for much gas before a high pressure is reached, so that the flow of acid is stopped gradually and without excessive strain on the apparatus. To guard against any possible forcing of the acid back into (C), enough mercury is put in the bulb tube to fill the lower bend. It offers but little resistance to the flow of the acid, since it spreads out in the bulb, but when it is forced back into the narrow vertical part of the tube it adds materially to the opposition to be overcome in driving the acid from the tube back into the acid reservoir.



To guard against any possible forcing of the acid back into (C), enough mercury is put in the bulb tube to fill the lower bend. It offers but little resistance to the flow of the acid, since it spreads out in the bulb, but when it is forced back into the narrow vertical part of the tube it adds materially to the opposition to be overcome in driving the acid from the tube back into the acid reservoir.

The height at which the acid reservoir is placed depends on the pressure desired. For ordinary work in the laboratory where the maximum pressure is that required to charge with hydrogen sulphide two ordinary five-pint bottles in series, three feet of vertical distance from the lower end of tube (c) to the lower end of tube (D) is about right. This is enough to balance the back pressure of the mercury and to insure rapidity of action against the maximum pressure mentioned. The acid reservoir is filled by

removing its upper stopper and tube, preferably after closing the pinch-cock on (*d*). The acid used in making hydrogen sulphide is crude muriatic acid diluted with two parts of water. The waste solution drips into (*B*) so nearly neutral that it is black with precipitating ferrous sulphide and so dilute that there is no danger of any salt crystallising out. It is removed by opening the pinch-cock on the tube (*E*), when the pressure in the generator forces it out into the beaker or other vessel placed to receive it. The cylinder (*A*) is filled by removing its rubber stopper after closing the pinch-cock on (*d*). Its contents should not be finely broken, that is, it is best to reject all which will pass through a sixteen-mesh sieve. Perhaps a good average size is that of peas. The material is supported by a piece of coarse iron wire gauze on which the exhausted acid has little, if any, action.

The chemical building of the University of Wisconsin has a special room in the basement, in which hydrogen sulphide is generated and operations may be performed requiring large use of that gas. From this room lead pipes extend to fume closets in each of the two principal laboratories, where they terminate in a row of gas-cocks with small openings. With the above described apparatus connected with this pipe system a student has only to attach his glass tube to one of the gas-cocks and open it a sufficient amount to let the hydrogen sulphide flow at the desired rate. On completing his precipitation or saturation he has only to shut off the gas and detach. In connection with this large pipe system there is one peculiar difficulty. When the waste solution is drawn off at (*E*) the pressure in the generator may be so much lowered that the water in an ordinary wash-bottle would be forced into the generator by the pressure in the pipes. To obviate this two wash-bottles are used, so placed that the longer tubes of each are connected together. Of the shorter tubes one is connected with the generator and one with the pipe system. The bottle nearest the pipes is the real wash-bottle and ordinarily contains the wash-water, but this is emptied into the other bottle without harm done whenever the pressure in the generator is less than that in the pipes.

The apparatus is made and can be obtained of Mr. Emil Greiner of New York.

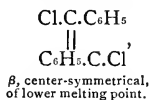
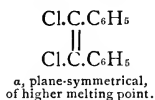
That it may work perfectly it must not leak, and consequently must be well made to resist the considerable pressure to which its joints are subjected.

ON THE CHLORINE COMPOUNDS OF TOLANE.

BY ARNOLD EILOART.

The Two Tolane-dichlorides.

For the stereo-chemical formulae for these two compounds,



experimental proofs have already been offered by Blank.¹ These proofs depend on the relative quantities of the two chlorides which result from the reduction of the tetrachloride with zinc dust and alcohol. The present investigation was carried out in the laboratory of Professor Wislicenus, at his suggestion, for the purpose of further testing these formulae, by determining (1) the relative stability of the two chlorides, (2) the possibility of the production of one or both of the chlorides by the chlorination of tolane. For the theory of Wislicenus² not only declares that there must be between these isomers a considerable difference in stability, but enables us to foretell that only that modification which may prove to be the less stable can be formed directly and without any intermediate product by the simple addition of chlorine to tolane. In the first place, therefore, with a view to comparing the relative stability of the chlorides, quantitative investigations were made (1) as to their behavior at high temperatures, (2) as to their resistance to the reducing action of zinc dust.

Preparation of the Tolane-dichlorides.

These were made from tolane-tetrachloride, which was prepared at first by the method indicated by Hanhart³ and worked out by Blank, by treating benzotrichloride, diluted with benzene, with reduced copper. The product of the action, after concentration, consisted chiefly of a black tarry mass, from which the crystals it contained could be separated only with great difficulty. To obtain a better result I now tried the experiment without the benzene,

¹ Ann. Chem. (Liebig) **248**, 17.

² Joh. Wislicenus: Ueber die räumliche Anordnung der Atome in organ. Molec. Leipzig, 1887.

³ Ber. d. chem. Ges. **15**, 898.

heating the copper with the benzotrichloride alone, and varying the time, the temperature, and the proportion of the substances. These experiments enabled me to confirm the observation of Hanhart, who noticed a very violent reaction between the copper and the benzotrichloride, accompanied by evolution of fumes and by rise of temperature. Onufrowicz,¹ on the other hand, remarks that in his experiments the reaction went quite quietly. The phenomena observed by Hanhart repeated themselves in my experiments, although not till the temperature reached 105° C. That the temperature of the water-bath was not, as in Hanhart's case, sufficient was due probably to a difference in the reducing power of the copper employed. Still the yield remained very unsatisfactory, and finally, to use up the tarry residues, they were distilled under diminished pressure, and in this way the tolane-dichlorides were obtained at once, although in no great quantity.

The tetrachloride was now prepared from benzil. It proved best to add at once the excess of phosphorus pentachloride necessary for the formation of the tolane-tetrachloride, and not first to prepare the dichlorbenzil. Even in this way the latter was formed in considerable quantity, as was proved by the melting point and by the percentage of chlorine in the by-product.

0.2807 gram substance gave 0.3088 gram AgCl.

	Theory for $C_6H_5.CO.CCl_2.C_6H_5.$	Found.
Cl	26.8	27.17

When allowed to crystallise slowly from petroleum ether, the dichlorbenzil formed beautiful transparent plates, with oblique angles, and easily to be obtained 2 cm. long.

From 88 grams benzil 44 grams of nearly pure tetrachloride were at once obtained. For recrystallising it petroleum ether (b. p. 110°) is to be recommended. This, when hot, dissolves the tetrachloride much more freely than does alcohol, and when cold dissolves much less than does benzene.

To prepare the tolane-dichlorides from the tetrachloride and to separate them from one another, the method detailed by Blank was followed. The separated dichlorides were then recrystallised from alcohol until the melting points were constant. The plane-symmetrical chloride fused then at 139.5°, which agrees with Hanhart's observation, while Zinin² and Limpricht and Schwan-

¹ Ber. d. chem. Ges. **17**, 833.

² Ibid. **4**, 289.

ert¹ found 153°, and Liebermann and Homeyer,² Onufrowicz (l. c.) and Blank found 143°. The center-symmetrical chloride fused at 58°; Hanhart gives 60°, other authors 63°.

Behavior of the two Dichlorides when heated.

Zinin³ distilled these substances and only mentions that they come over undecomposed. According to Limpricht and Schwantert (l. c.), each chloride is, on distillation, partially converted into the other. Blank⁴ states that, whichever of the two chlorides be distilled, the composition of the distillate is the same; it contains, namely, seven parts of the center-symmetrical to three of the plane-symmetrical. And Blank says:

"This is to be accounted for by the application of Wislicenus' explanation of the conversion by heat of unsaturated compounds into compounds geometrically isomeric. As soon as the heat loosens the bonds of the atoms in the molecule, one chloride can turn into the other. Then, of course, the molecules of the more favored form, *i. e.* those having the axis- (\equiv center-) symmetrical form, will be found in greater number than those of the plane-symmetrical configuration, and the relative proportion of the two forms will alter with the temperature, but for any particular temperature will be constant."

The question was to subject to an exact test these dicta of the theory.

For heating the substances a vapor-oven of copper was used. With this the temperature in the inner air-space could be kept constant for hours within half a degree. The vapors of boiling cumene (b. p. 153°), aniline (b. p. 183°) and benzoic ether (b. p. 213°) were used in succession. The experiments were conducted throughout in the same way. Into a small, thin-walled tube, closed at one end, were weighed exactly 2 grams of the one chloride, and into a similar tube 2 grams of the other; the tubes were then put each into a thick-walled one, and the latter sealed. The sealed tubes were then laid side by side in the oven. This had already been heated to constant temperature. Opening it lowered this temperature, and the time of heating was reckoned from the moment when the original temperature was restored. After cooling, the contents of each tube were brought by means

¹ Ber. d. chem. Ges. 4, 379.

² Jahresbericht, 1871, 438.

³ Ibid. 12, 1971.

⁴ Ann. Chem. 248, 18.

of 20 grams absolute alcohol into an Erlenmeyer flask, and dissolved with the aid of heat. Any crystals which separated out on cooling were collected on a weighed filter, and washed with about 10 grams alcohol. The filtrate was always evaporated to apparent dryness in a weighed Erlenmeyer flask, placed aslant on the water-bath. The residue in the flask was then left to stand *in vacuo* over sulphuric acid, together with the crystals on the weighed filter. If the flask be left on the water-bath after the alcohol odor has disappeared, some of the solid contents volatilise. Accordingly the residue, after being weighed, was warmed only till it melted, in order to expose a fresh surface for the evaporation of all traces of alcohol. The flask was then left again in the desiccator from which the air had been exhausted. The melting and drying in the desiccator were repeated till the weight was constant.

On the filter remained now only the slightly soluble α - or plane-symmetrical dichloride, the weight of which is shown in Table I, Col. 6; the residue from the filtrate consisted mostly of the easily soluble β - or center-symmetrical chloride, but contained also some α -chloride, the amount of which was yet to be determined. To this end the weight of the alcoholic filtrate was always taken (Table I, Col. 4), and by subtracting from this the weight of the dried residue, the weight of the alcohol to be considered was arrived at. But the solubility of the plane-symmetrical chloride in pure alcohol is quite different from its solubility in alcohol containing center-symmetrical chloride. The results given in Table I are therefore only, preliminary.

TABLE I.

	1.	2.	3.	4.	5.	6.	7.
Experiment.	Taken.	Time.	Temp.	Alcoholic filtrate.	Residue from filtrate.	On filter.	Total Col. 5 + Col. 6.
I. { Plane, 2 gr. Center, 2	2	2 hours.	{ 143° — 177 }	25 gr. 20	0.1444 dissolved everything.	1.8498	1.9942
II. { Plane, 2 Center, 2	2	2	177	21.43 20	0.1937 dissolved everything.	1.7989	1.9926
III. { Plane, 2 Center, 2	2	3	177–204	29.20 33.49	0.7494 1.7533	1.2419 not determined.	1.9913
III ^a . { Plane, 2 Center, 2	2	3	204	27.16 28.07	0.7954 0.7405	1.2041 1.2391	1.9995 1.9766
IV. { Plane, 2 Center, 2	2	10	206	34.5 29.0	1.3316 1.5102	0.6430 0.4729	1.9746 1.9831
IV ^a . { Plane, 2 Center, 2	2	10	204½	36.13 33.14	1.3664 1.5400	0.6204 0.4372	1.9868 1.9772
V. { Plane, 2 Center, 2	2	slowly distilled.	265–350 +	30.07 28.22	1.4531 1.4741	0.5330 0.5061	1.9861 1.9802
V ^a . { Plane, 2 Center, 2	2	distilled very fast.		30.47 29.79	1.3593 1.4445	0.6353 0.5369	1.9946 1.9814

The table shows that the sum of the weights of the products obtained is in nearly every case rather less than the weight of substance taken. Nevertheless no appreciable decomposition had taken place, for even at the highest temperatures the product after heating was but slightly colored, and on opening the tube neither pressure nor escape of gas was to be noticed. Besides, the weight of the tube and contents remained unaltered on opening.

There was, however, a source of loss detected. After the residue from the alcoholic filtrate had attained constant weight, alcohol was added till the solution had again the weight of the original filtrate. The weight of the residue left, on again evaporating, was always a few milligrams less than before, and this number of milligrams, representing the chloride which had volatilised with the alcohol, is therefore to be added to the weight originally found. Thus in the last experiment (V^a , Table I), starting with the plane-symmetrical chloride, the sum of the weights of the dissolved and of the undissolved portions obtained was 1.9946 gram. To the dried dissolved portion alcohol was added till the weight was that of the original filtrate, 30.47 grams. After evaporating the alcohol the weight of the residue was 0.0053 gram less than at first: $1.9946 + 0.0053 = 1.9999$. Starting with the center-symmetrical chloride, the corresponding figures were $1.9814 + 0.0104 = 1.9918$. So that the unavoidable loss is very small.

And the loss by volatilisation can affect only the center-symmetrical chloride, for the amount of the plane-symmetrical chloride contained in the filtrate is arrived at quite independently. And since the determinations of the plane-symmetrical chloride proved more exact of execution than those of the other, the amount of change was calculated only from the former, while the weight of the dissolved portion served as a control.

On the separate experiments given in the table the following remarks may be made:

Experiment I.—As the α -chloride did not fuse when heated in cumene-vapor, the heating of both chlorides was continued with aniline-vapor.

Experiment III.—After heating an hour with aniline-vapor (since Experiment II showed so little change at this temperature), the heating was continued in the vapor of benzoic ether. From the solution of the β -chloride, the less soluble product appeared this time not in one of the known forms of the α -chloride crystals,

in oblique-angled plates, or in nitre-like columns, but in needles, such as the center-symmetrical chloride forms, but more pointed and harder than these. On this account the determination of the undissolved portion was in this experiment given up, and the substance was subjected to further examination. After washing with alcohol the slightly soluble crystals fused, without any recrystallisation, at 138° —almost at the melting point of the plane-symmetrical chloride. Under the microscope not a single crystal of prismatic form could be seen among the needles. The small quantity which was left after washing was now used for a chlorine determination.

0.0733 gram substance heated to 220° four hours in a sealed tube with AgNO_3 and HNO_3 gave 0.086 gram AgCl .

	Theory for $\text{C}_{14}\text{H}_{10}\text{Cl}_2$.	Found.
Cl	28.51	29.02

In Experiment IV exactly similar needles were found in larger quantities; their solubility was nearly the same as that of the plane-symmetrical chloride.

	Alcohol.	Dissolved.	Dissolved by 100 grs. alc.	Temp.
Needles	26.361 grams	0.149 gram	0.565	19°
Plane-chloride { (1)	47.401 "	0.2763 "	0.583	
(plates) { (2)	40.087 "	0.2332 "	0.582	

In fact these needles change on recrystallisation and even on simply standing with alcohol, into the ordinary oblique-angled plates. They are accordingly nothing but plane-symmetrical chloride. Later this chloride, when obtained from solutions which contained much of its isomer, appeared always in this form, and sometimes the needles were 2 cm. long.

Experiment V.—Of each chloride 3 grams were distilled successively, the same air-bath and distilling flask being used for each. The temperature was kept as low as possible; with both chlorides it varied between 265° and over 350° . At first the chlorides came over white, later yellowish. From 3 grams of the center-symmetrical I obtained 2.66 grams, from 3 grams plane-symmetrical 2.81 grams of distillate. Of each distillate 2 grams were used for analysis, as shown in the table.

Experiment V^a.—2.6 grams center-symmetrical chloride distilled from the air-bath as quickly as possible, and without taking the temperature, gave 2.47 grams; and 2.6 grams plane-sym-

metrical chloride gave 2.43 grams of distillate. In both cases the distillate was white. Again 2 grams of each distillate were used.

Now before we can review the outcome of these experiments as a whole, each result must be subjected to the correction for the amount of plane-symmetrical chloride dissolved by the alcohol.

Solubility of the Tolane-dichlorides in Alcohol.

Determinations were made as follows:

	Alcohol, grams.	Dissolved, gram.	Dissolved by 100 grs. alcohol.	Temp.
Plane-symm. chloride	48.371	0.3437	0.710	24.4°
Center-symm. chloride	4.492	0.4721	10.51	
Plane- and center-symm. chlorides together	3.827	0.4182	10.93	25.6°

If we add to the amount of plane-symmetrical chloride dissolved at 24.4°, the amount of center-symmetrical dissolved at the same temperature, we find the sum ($0.71 + 10.51 = 11.22$) to be .29 per cent. higher than the amount of the mixed chlorides which is dissolved even at the temperature 25.6°.

Had this diminution of solubility been divided between the two chlorides in the proportion of their solubilities, only a small part of it would have fallen on the plane-symmetrical chloride. But that this was the chloride whose solubility was chiefly affected was proved as follows. To a saturated solution of center-symmetrical chloride was added a little less of the other than the alcohol alone would have dissolved. By warming complete solution was effected. On cooling, although the balance showed that there had been practically no loss of alcohol, crystals separated out. Their solubility (unwashed) was but little greater than that of the plane-symmetrical chloride.

	Alcohol, grams.	Dissolved, gram.	Dissolved by 100 grs. alcohol.	Temp.
The crystals	1.278	0.012	0.939	27°
Plane-symm. chloride	28.792	0.2085	0.724	

The converse experiment was made by dissolving in alcohol saturated with the plane-symmetrical chloride and then warmed, rather less of the other chloride than the alcohol when cold would have dissolved. After cooling, alcohol was added to make up the slight loss of weight due to evaporation. The solubility of the crystals which separated out was determined.

Alcohol.	Dissolved.	Dissolved by 100 grams alcohol.	Temp.
1.491 gram	0.0123 gram	0.825	23.3°

This quantity of alcohol would dissolve 0.0106 gram of pure plane-symmetrical chloride or only 1.7 mgm. less.

The remarkable manner in which the solubility of the less soluble was lowered by the presence of the more soluble chloride led me to estimate the proportion of the plane-symmetrical chloride so thrown out of solution. It was found that from a saturated solution of plane-symmetrical chloride more than 56 per cent. of it was precipitated by the addition of center-symmetrical chloride.

Next, in order to eliminate from my results the effects of this varying solubility, mixtures of the two chlorides in known proportion were made, and these were treated exactly as the unknown mixtures had been treated in order to separate their components. The sum of the two chlorides was always two grams, and the proportions were so chosen that the weight of the chloride left on the filter in each experiment should be nearly the same as in one of the previous experiments. In these, as in the previous separations, the same temperature, 19° C., was closely adhered to; and here, too, 20 grams alcohol were used for dissolving and about 10 grams for washing. The filtrate was weighed in each experiment, and from this weight was deducted the weight of the residue left on evaporation. In Table II the weight of the plane-symmetrical chloride taken is given under *a*, and under *b* that of the residue on the filter. In every case *a* was mixed with $(2 - a)$ grams of the other chloride. The weight of the alcohol in the filtrate is called *B* and the product $\frac{a-b}{B} \cdot 100$, or the amount of the plane-symmetrical chloride dissolved by 100 grams alcohol is called *S*.

TABLE II.

Experiment.	<i>a</i> .	<i>b</i> .	<i>a-b</i> .	<i>B</i> .	<i>S</i> .	<i>S</i> mean.
I. { 1	0.3333	0.264	0.0693	28.07	0.2469	} 0.246
2	0.3333	0.270	0.0633	25.85	0.2449	
II. { 1	0.6666	0.5481	0.1185	31.10	0.381	} 0.374
2	0.6666	0.5680	0.0986	26.90	0.367	
III. { 1	1.3333	1.204	0.1293	29.69	0.4355	} 0.440
2	1.3333	1.218	0.1153	25.91	0.4450	

With the values of *a* as abscissae, and those of *S* as ordinates, these results are represented in the curve below. Besides passing

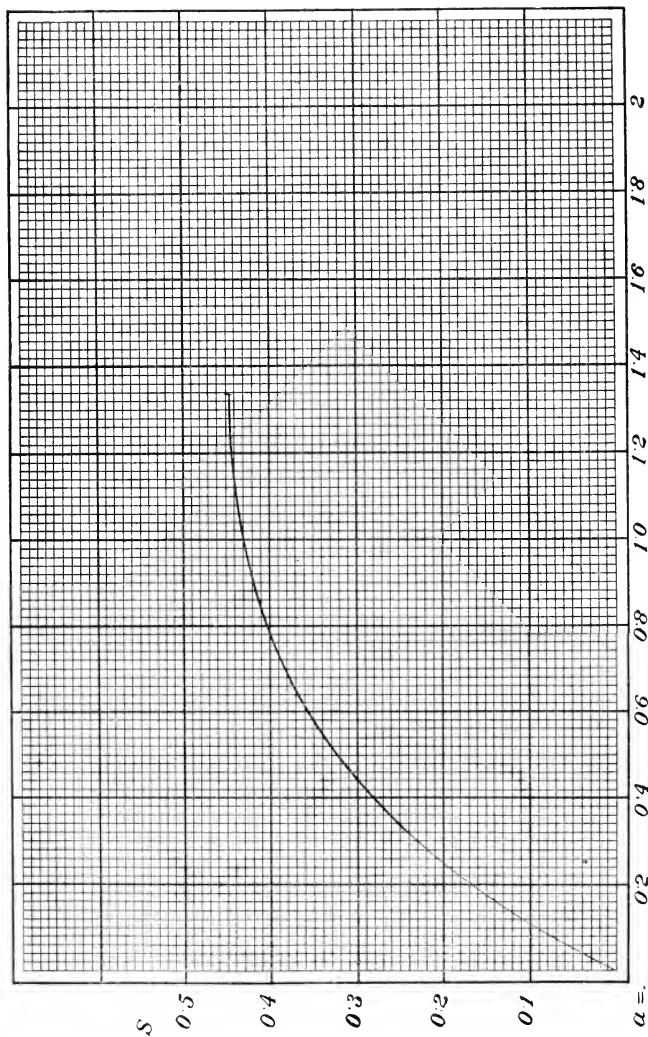
through the points indicated by Table II, the curve must of course pass through the origin of the system.

Table III shows the results of Table I corrected for the solubilities indicated by the curve. But the proportions of the known mixtures were so chosen that even without applying the curve the directly determined coefficients of solubility would suffice for a close approximation, except in the case of Experiment "IV^a (Center)," where the difference would be 0.013 gram. In the table, Col. 1 gives the plane-symmetrical chloride weighed on the filter (= Col. 6, Table I), *S* is the coefficient of solubility indicated by the curve for each mixture, *B* the weight of alcohol in the filtrate, and therefore $\frac{S \times B}{100}$ is the weight of the plane-symmetrical chloride dissolved. For the reasons given, the amount of chloride changed is reckoned from the weight of plane-symmetrical chloride obtained. This final result of the series of experiments is given in Col. 8 as "Conversion per cent.," *i. e.* the percentage of altered substance.

TABLE III.

Experiment.	1 On filter.	2 <i>S</i> .	3 <i>B</i> .	4 $\frac{S \times B}{100}$.	5 Plane chloride (Col. 1 + Col. 4).	6 Time.	7 Temp.	8 Con- version per cent.
II. { Plane,	1.7989	0.582	21.24	0.1236	1.9225	2 h.	177°	3.88
Center,			20 dissolved	everything.				
III. { Plane,	1.2419	.440	28.45	.1252	1.3671	3	177°-204°	31.65
Center,								
III ^a . { Plane,	1.2041	.440	26.46	.1164	1.3205	3	204°	33.98
Center,	0.2391	.230	27.33	.0628	0.3019			
IV. { Plane,	0.6430	.393	33.17	.1303	0.7733	10	206°	61.34
Center,	0.4729	.353	27.49	.0970	0.570			
IV ^a . { Plane,	0.6204	.388	34.76	.1348	0.7552	10	204½°	62.24
Center,	0.4372	.333	31.60	.1052	0.5424			
V. { Plane,	0.5330	.368	28.62	.1053	0.6383	slowly distilled.	265-350+	68.09
Center,	0.5061	.359	26.75	.0961	0.6022			
V ^a . { Plane,	0.6353	.388	29.11	.1129	0.7482	distilled very fast.		62.59
Center,	0.5369	.368	28.35	.1043	0.6412			

From the last three columns it is at once evident how with both chlorides the conversion of one into the other increases with the temperature and with the time, and how this conversion attaining a maximum leaves only 31.91 per cent. of the plane-symmetrical chloride unchanged (Experiment V), while of the center-symmetrical chloride only 32.06 per cent. are changed (Experiment V^a);



Curve showing the solubility, S , in grams per 100 grams alcohol, of the plane-symmetrical tolane-dichloride when a grams of it

the conversion being thus, within 0.15 per cent., complementary for the two chlorides, so that the final products from both have the same composition.

The whole series of experiments places it beyond all doubt that, as the theory of Wislicenus declares, the center-symmetrical chloride is far more stable than its isomer.

That the two chlorides when heated in the same way did not yield distillates of the same composition is to be accounted for by the fact that they do not distill at the same temperature. For according to Hanhart (l. c.), the plane-symmetrical chloride boils at 260° – 280° , and the other at 310° – 313° . They must therefore be distilled at different temperatures if we wish to expose them for the same time to the heat. Accordingly we must compare not the two experiments "V Plane" and "V Center," but "V Plane" and "V^a Center."

By calculating for the different pairs of results the ratio of the altered chlorides, which is the same as the ratio of the velocities with which they change into one another, we obtain in every case almost the same figures.

From Table III, Column 8, we have:

	III ^a .	IV.	IV ^a .
Altered Plane,	33.98	61.34	62.24
Altered Center,	15.09	28.5	27.12
Ratio $\frac{\text{Plane}}{\text{Center}}$,	2.25	2.15	2.29
Mean,	2.23		

But for the reasons just mentioned, we must compare "V Plane" with "V^a Center," and "V^a Plane" with "V Center."

	V Plane, V ^a Center.	V ^a Plane, V Center.
Altered Plane,	68.09	62.59
Altered Center,	32.06	30.11
Ratio $\frac{\text{Plane}}{\text{Center}}$,	2.12	2.07

Indeed, from the three experiments conducted at 204° we can calculate within one per cent. the maximum attainable conversion, *i. e.* the composition of the product when the *equilibrium mobile* is established. For the mean value 2.23 calculated above for the

ratio $\frac{\text{Plane}}{\text{Center}}$ at 204° corresponds to

69.04 per cent. Plane and 30.96 per cent. Center,
the maximum found being

68.09 per ct. (V Plane) and 32.06 per ct. (Vⁿ Center).

Difference 0.95

1.1

And this in spite of the fact that in the latter experiments a change of state had taken place, and that as the distillations were completed in two or three minutes, the velocities of conversion were several hundred times greater in them than in the experiments at 204° ; still the ratio of the velocities remained almost constant.

But in this case where the alteration of the coefficient of equilibrium α (*i. e.* the ratio of the velocities of conversion) due to change of temperature is zero, the heat of conversion, ς , is also zero, according to the equation given by Van't Hoff,¹

$$\frac{d(\alpha)}{dT} = \frac{\varsigma}{0.02 T^2}.$$

Within the limits of error of these experiments, then, there is in the change of the tolane-dichlorides into one another neither development nor absorption of heat, and the heat of combustion must be for both chlorides nearly the same.

Further, we can to some extent compare the effects of an increase of temperature on the chlorine atoms in the molecules of the two chlorides. If we call the distance between the two chlorine atoms in the one molecule x , and in the other y , and let these be the values for a certain definite temperature, while $x + b$ and $y + b'$ are the values for another definite temperature; then, since the ratio of the velocities of conversion remains the same at different temperatures, and since this ratio would vary if the ratio of the distances between the chlorine atoms in the two molecules varied (unless, indeed, the effect of such variation should be eliminated by compensating variations in the distances of other atoms), we have

$$\frac{x}{y} = \frac{x+b}{y+b'} \text{ and } \frac{x}{y} = \frac{b}{b'}$$

And if $x \pm y$, which according to the theory of geometric isomerism would hold in the case of the chlorine atoms, then $b \pm b'$. Either, therefore, the oscillations of the chlorine atoms in the

¹ Cf. Ostwald, *Lehrbuch der allgemeinen Chemie* 2, 737.

molecule of the one chloride, caused by rise of temperature, are unequal to those of the chlorine atoms of the other, caused by the same rise of temperature, or these oscillations make no appreciable difference in the distances between the atoms, i. e. b and b' vanish in comparison with x and y .

Bearing of the Experiments described on the Results obtained by Blank.

In view of the remarkably variable solubility of the plane-symmetrical chloride proved above, it is evident that those of Blank's results,¹ in which this solubility comes into consideration, require a correction. Blank added ethyl alcohol (in some experiments amyl alcohol) to 20 grams tolane-tetrachloride and reduced with zinc dust. He determined the quantities of the dichlorides so obtained and comments thus on the results :

"If we consider the numbers obtained for the plane-symmetrical chloride, we find that according to the theory they are too high. Since, as already explained, tolane-tetrachloride can have for every two molecules of the more favored configuration [of the space-formula] at most only one molecule of the less favored, and since 20 grams tolane-tetrachloride correspond to 15.56 grams dichloride, there should be formed at most $\frac{15.56}{3} = 5.19$ grams of plane-symmetrical chloride ; but at 80° and at 130° this limit is exceeded."

Now in these experiments about 200 cc. or 160 grams alcohol were used for dissolving the chlorides, and the plane-symmetrical chloride contained in this was calculated as if its solubility had been the same as in alcohol containing no center-symmetrical chloride. At the temperature of these experiments, 160 grams of pure alcohol dissolved, according to Blank, 1.08 gram or 0.675 per cent. plane-symmetrical chloride. The temperature is not mentioned ; but still my experiments render possible an approximate correction. For, at the temperature at which I found the solubility of the plane-symmetrical chloride *per se* to be 0.582 per cent., the solubility of the plane-symmetrical chloride, when mixed with twice its weight of center-symmetrical chloride, was only 0.374 per cent. At the temperature then at which Blank found the solubility of the plane-symmetrical chloride *per se* to be 0.675

¹ Loc. cit. p. 27.

per cent. ($=0.582 + 0.093$), the solubility of the plane-symmetrical chloride, when he had it mixed with twice its weight of center-symmetrical chloride, could not have been *more* than $0.374 + 0.093 = 0.467$ per cent.

It may be objected that my coefficients of solubility, although available for the correction of my own experiments, must be too low, since part of the alcohol was used only for washing, and was not left 24 hours in contact with the substance, as was the case in Blank's work. But this does not cause low results. The alcohol used for washing, being free from center-symmetrical chloride, dissolves proportionally more of the plane-symmetrical chloride than does alcohol left 24 hours in contact with the mixed chlorides. Thus two mixtures of $1\frac{1}{2}$ gram center- with $\frac{2}{3}$ gram plane-symmetrical chloride gave, after separation with alcohol in the usual way, residues of the latter chloride which were thoroughly freed from center-symmetrical chloride, and on further washing yielded filtrates consisting of:

I. 10.075 grams alcohol and 0.0478 gram chloride.

II. 10.042 grams alcohol and 0.044 gram chloride; or 100 grams alcohol dissolve, I. 0.474, II. 0.438; whereas in Table II the solubility of the plane-symmetrical chloride in the presence of twice its weight of center-symmetrical chloride is only 0.374 per cent.

Accordingly, we may take as stated 0.467 per cent. as more than the maximum that could have been dissolved in Blank's experiments. The degree of concentration was almost exactly the same in his experiments as in mine. In the latter there were, before the washing with alcohol, which we have already taken into consideration, in 20 grams alcohol $1\frac{1}{2}$ gram center-symmetrical chloride, or 6.66 per cent., and half that quantity of plane-symmetrical chloride; in the former there were in 160 grams alcohol about 10.37 grams $\left(\frac{15.56}{3} \times 2\right)$ or 6.48 per cent. center-symmetrical chloride, and half that quantity of plane-symmetrical chloride. Accordingly the quantity of plane-symmetrical chloride dissolved from such a mixture by 160 grams alcohol could not be more than $160 \times 0.467 = 0.747$ gram.

Let us apply this figure to Blank's results.

In his paper these stand thus:

Taken 20 grams tolane-tetrachloride.

I. At 80° C.	(1).	Plane-sym. chloride separated,	. 4.2	grams.
		Dissolved in 200 cc.,	1.08
		Total,	5.28
	(2).	Plane-sym. chloride separated,	. 4.31	
		Dissolved in 200 cc.,	1.08
		Total,	5.39

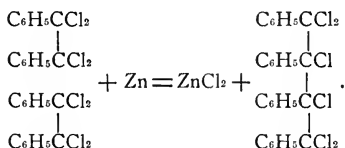
Corrected, they stand thus :

I. At 80° C.	(1).	Plane-sym. chloride separated,	. 4.2	grams.
		Dissolved in 200 cc. alcoholic		
		solution of center-sym.,	. .	0.75
		Total,	4.95
	(2).	Plane-sym. chloride separated,	. 4.31	
		Dissolved in 200 cc. alcoholic		
		solution of center-sym.,	. .	0.75
		Total,	5.06

Theoretical maximum, 5.19 grams.

Hence the theoretical limit is at 80° C. certainly not exceeded. How far a similar correction would alter the somewhat higher results obtained with amyl alcohol is matter for further experiment. If they should be lowered to the same extent, they too would, within the limits of error of the experiments, coincide with the theoretical number.

Such a simple explanation of the discrepancy between the results and the theory is the more satisfactory, because the explanation given by Blank cannot be accepted as final. This explanation depends on the formation, in the reduction of the tolane-tetrachloride, of an intermediate product, "ditolane-hexachloride." Its formation is represented, according to Blank, by the equation



Now since, as Blank found, one molecule of the plane-symmetrical chloride can unite with one molecule of tolane-tetrachloride to form the hexachloride, it would not be surprising if, in spite of the careful manner in which the whole series of Blank's experiments was carried out, a little tetrachloride, converted in this way into hexachloride, had been weighed with the plane-symmetrical chloride, especially since the solubility of the hexachloride is, as will be shown later, almost the same as that of the plane-symmetrical chloride.

Blank's explanation is, however, quite different. The hexachloride, as he shows, yields, on further reduction, more plane- than center-symmetrical chloride, and to this he attributes the excess of plane-symmetrical chloride obtained from the tetrachloride.

"The formation," says Blank, "of the hexachloride from the tetrachloride does not take place quantitatively. If we allow just so much zinc dust to act on the latter as suffices for its decomposition, we get from 20 grams tetrachloride about 9.3 grams hexachloride, together with 7.4 grams of the axial-symmetrical chloride, *i. e.* to one molecule of hexachloride about two of dichloride. In this reaction no plane-symmetrical chloride whatever is formed. Only through the further action of zinc dust do we get the latter, and 10 grams hexachloride gave (I) 6 grams, (II) 5.9 grams plane-symmetrical chloride" (l. c. p. 29).

According to this the 9.3 grams hexachloride obtainable from 20 grams tetrachloride would yield 5.53 grams plane-symmetrical chloride. So that when the formation of the hexachloride is favored to the utmost (*cf.* Blank, l. c. p. 28), even then the theoretical limit, 5.19 grams, for the plane-symmetrical chloride is exceeded by only 0.34 gram. This hardly explains the fact that in an experiment (l. c. p. 27) conducted without adherence to the conditions favorable to the formation of hexachloride, the theoretical limit for the plane-symmetrical chloride was still further exceeded, *viz.* at 130° by 0.46 gram.

But Blank supports his explanation for the excessive yields of plane-symmetrical chloride by theoretical reasons also. The space-formula of the hexachloride proves, he says, that this must yield on reduction more plane- than center-symmetrical chloride. That the hexachloride is a homogeneous body, that it has in fact only one space-formula, is, however, not yet proved. Such a view

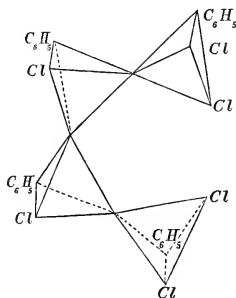
is contradicted by the result of a determination of its molecular weight conducted by Blank according to Raoult's method. With regard to this determination Blank says: "This result would indicate, since there can be no tolane-trichloride, that the hexachloride is not a homogeneous compound, but a mixture of tolane-di- and tetra-chloride crystallising together. But several of the chemical facts which have been mentioned are opposed to this idea, more particularly the formation of this body out of *both* the dichlorides by the action of chlorine or on treatment with the tetrachloride. Since these facts carry more weight than the result of Raoult's method, which has not yet been proved applicable to every class of substances,¹ the substance investigated must be accounted homogeneous and described as ditolane-hexachloride" (l. c. p. 33). In the experiment with chlorine, which was passed into the fused chlorides, the temperature is not given. But the process is a complicated one; "there are formed together with oily liquids certain quantities of ditolane-hexachloride," and the possibility of the conversion of the chlorides one into the other is not excluded.

On treatment with the tetrachloride, the formation of the hexachloride from the center-symmetrical chloride did not result, as was the case with the plane-symmetrical chloride, through merely heating the alcoholic solution of the two bodies, but the substances had to be heated for half an hour at 180° , a temperature, according to Blank, "at which the dichlorides do not begin to change one into the other." But, according to my experiments, the temperature at which the two chlorides begin to change one into the other is 177° or lower, and at 180° it is quite possible that even in half an hour in presence of the tetrachloride, if this takes up every trace of plane-symmetrical chloride as fast as it is formed, removing it from the sphere of action, considerable quantities of the latter might be formed, and thus cause the formation of hexachloride.

But however the solid hexachloride may be constituted, it follows, from reasons presently to be given, that the hexachloride dissolved in alcohol, as well as (according to the lowering of the freezing point) that dissolved in benzene, behaves like a mixture of plane-symmetrical chloride and tetrachloride.

¹ But we are indebted to Blank himself for the successful application of Raoult's method to the tolane-dichlorides, which surely belong to the same class of substances with the hexachloride.

But suppose the hexachloride dissolved in alcohol to possess the space-formula given by Blank. The explanation based on this is still unsound. Giving four configurations of the formula as possible, Blank describes three as yielding plane- and center-symmetrical molecules in equal numbers, while one yields plane-symmetrical molecules only. But the configuration which gives plane-symmetrical chloride only,



is just the least favored of all; for here, in every case, negative components (chlorine atoms) stand opposite negative, and positive components (phenyl groups) opposite positive in corresponding positions. Now, even if the temperature should be high enough to cause this configuration to occur as frequently as each of the three more favored ones, we should still have from the four configurations only five molecules of plane- to three molecules of center-symmetrical chloride, whereas the proportion actually found was more than two to one.

I here give the quantities obtained by Blank, together with the figures calculated according to this application of his theory.

Reduced : 10 grams ditolane-hexachloride.

	I.	Found.	II.	Theory for 5 plane to 3 center.
Plane-sym. chloride, . .	6.0		5.9	5.45
Center-sym. chloride, . .	2.7		2.9	3.27

I now offer a more simple explanation of the facts.

Not only the ratio of one to two just referred to, but also the circumstance that "the formation of the hexachloride from the

tetrachloride does not take place quantitatively"; that "from 20 grams tetrachloride we get about 9.3 grams hexachloride, together with 7.4 grams of the axial-symmetrical chloride, *i. e.* to one molecule of hexachloride about two of dichloride"; moreover, that "in this reaction no plane-chloride whatever is formed"; all these facts and figures are explained by the hypothesis rejected by Blank, that the hexachloride is a mixture of tetrachloride and dichloride (plane-symmetrical, to wit) crystallising out together; so that in the reduction of the tetrachloride with zinc, the hexachloride results only from the union of the tetrachloride with plane-symmetrical chloride, and therefore only so many molecules of hexachloride can be formed as there were molecules of plane-symmetrical chloride formed beforehand; whence follows that the quantity of plane-symmetrical chloride formed by dechlorination of the tetrachloride cannot be increased, but only diminished by the formation of hexachloride; and therefore it was that with a maximum yield of hexachloride "no plane-symmetrical chloride whatever was formed." This view explains at once why in the reduction of the tetrachloride there were formed two molecules of axial- (center-) symmetrical chloride to every one of hexachloride: simply because for every two molecules of center-symmetrical chloride there is formed one of plane-symmetrical, and this uniting with one molecule of tetrachloride gives one molecule of hexachloride.

Further, if the dissolved hexachloride represents a molecule of tetrachloride and a molecule of plane-symmetrical chloride, how would it behave when treated with zinc dust and alcohol, so as to form the dichloride from it? Exactly as the experiments show it does behave.

For simplicity let us consider three "molecules" of hexachloride as consisting of three molecules of plane-symmetrical chloride and three molecules of tetrachloride. The three former would remain unchanged. The three latter would yield as usual one molecule of plane- and two molecules of center-symmetrical chloride. Thus the three molecules of hexachloride would yield altogether four molecules of plane- to two of center-symmetrical chloride.

I here give the quantities obtained by Blank, together with the figures calculated on this theory.

Reduced: 10 grams hexachloride.

	Found.			Theory for 2 plane to 1 center.
	I.	II.	Mean.	
Plane-sym. chloride,	6.0	5.9	5.95	5.83
Center-sym. chloride,	2.7	2.9	2.8	2.92
	<hr/> 8.7	<hr/> 8.8	<hr/> 8.75	<hr/> 8.75

This is the strongest proof that ditolane-hexachloride does not exist in alcoholic solution as a homogeneous substance. In these figures, too, we again have evidence that the quantity of plane-symmetrical chloride has been over-estimated.

Action of Zinc-dust on the Tolane-dichlorides dissolved in Alcohol.

Zinin¹ observed that in this action tolane is formed. Liebermann and Homeyer,² by continuing the action for several days, brought the amount of chlorine which remained united with the tolane down to 6 per cent. Nowhere is anything said as to a quicker reduction of one chloride than of the other. But the theory of Wislicenus enables us to affirm that such a difference exists. For the chlorine atoms in the center-symmetrical chloride, held fast by their proximity to the phenyl groups, will not be so readily detached as will those in the plane-symmetrical chloride, which are in corresponding positions in the molecule. And in fact the difference is great, as the following experiments prove.

These experiments were conducted throughout in the same way. A solution of 1 gram center-symmetrical chloride in 150 grams alcohol was heated to boiling, the heat was removed and 2 grams of well purified zinc dust were immediately added. The solution was then kept boiling on the water-bath for a definite time, an inverted condenser being used; then the solution was quickly cooled and filtered at once from the zinc dust. The latter was washed with cold alcohol and dissolved in sulphuric acid. From this solution the chlorine (from any zinc oxychloride which might have been formed) was precipitated by silver nitrate. The chlorine was also precipitated in the alcoholic filtrate, and finally the two precipitates were weighed together. One gram of plane-symmetrical chloride was treated in exactly the same way.

Since in the first experiment no reduction had taken place, more zinc dust was prepared, and washed this time only once with hydrochloric acid, and then as before with water, alcohol and ether.

The results are here tabulated.

¹Jahresbericht, 1871, 438.

²Ber. d. chem. Ges. 12, 1871.

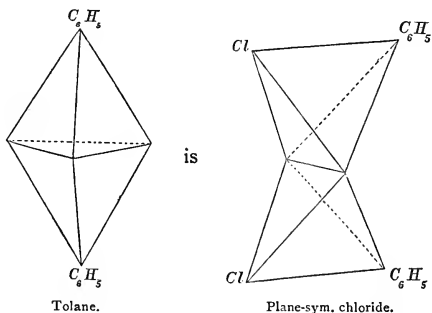
Reduction of the Tolane-dichlorides with Zinc-dust and Alcohol.

	Chloride.	Zinc I.	Time.	AgCl found.	=Chlorine.	Cl from Chloride.	Chloride Reduced.	per cent.
		2 grs.		0.0052	0.0013
I.	{ Plane, Center,	1 gr. 2 "	} 5 min.	0.0088	0.0022
		1 " 2 "		0.0106	0.0026
		Zinc II. 2 grs. 2 "		0.0206	0.0043
II.	{ Plane, Center,	1 gr. 2 "	} 3 hrs.	0.0144	0.0176	0.0133	0.047	4.7
		1 " 2 "		0.0714	0.0176
		1 " 2 "		0.0160	0.0039
III.	{ Plane, Center (a), Center (b),	1 gr. 2 grs.	} 10 hrs.	0.3918	0.0968	0.0925	0.325	32.5
		1 " 2 "		0.0770	0.0190	0.0139	0.049	4.9
		1 " 2 "		0.0704	0.0174

Thus in three hours no noticeable reduction of the center-symmetrical chloride had taken place, and in ten hours the reduction was hardly more than that effected in three hours in the case of the plane-symmetrical chloride. In both the action goes on faster after some time than at first.

The Products of the Chlorination of Tolane.

According to Liebermann and Homeyer (l. c.), on passing chlorine into a solution of tolane in chloroform, the tolane-dichloride fusing at 143° was produced. The theoretical explanation of this result is given in the treatise of Wislicenus already mentioned. For the only configuration which can result from the simple addition of two atoms of chlorine to



since whichever carbon-bond is broken the chlorine atoms can take only corresponding positions.

The experiments on this process are incomplete, but the results so far obtained thoroughly corroborate the theory. I repeated the experiment of Liebermann and Homeyer, using, instead of chloroform, pure carbon bisulphide (as little as possible) to dissolve the tolane. In a preliminary qualitative experiment the solution, cooled with ice and kept in the dark, was saturated with chlorine and left over night in an atmosphere of the gas. Then the carbon bisulphide was driven off by a stream of dry air. There remained a sticky, partly solid mass. This was dissolved in ten times its weight of hot alcohol. On cooling, the solution gave crystals amounting to about half the weight of the chlorinated product. After recrystallisation from alcohol the fusing point of the crystals was constant at 148° . They were short, thick, white prisms, of rhombic or quadratic appearance, and contained the same amount of chlorine as Blank's ditolane-hexachloride (fusing point 150°).

0.3043 gram substance heated 4 hours with HNO_3 and AgNO_3 to 220° , gave 0.4625 gram AgCl .

	Theory for $\text{C}_{28}\text{H}_{26}\text{Cl}_6$.	Found.
Cl	37.35	37.60

This ditolane-hexachloride seems to be identical with a body obtained by Limpricht and Schwanert¹ by heating tolane with phosphorus pentachloride to 170° . Their compound also crystallised in white prisms fusing at 150° , and "a chlorine determination indicated the composition $\text{C}_{14}\text{H}_9\text{Cl}_3$ " (L. & S.). The amount of chlorine found is not given; the theoretical amount for $\text{C}_{14}\text{H}_9\text{Cl}_3$ is 37.56 per cent.

The solubility of the hexachloride in alcohol was almost the same as that of the plane-symmetrical chloride.

Temp.	Alcohol.	Dissolved.	Dissolved by 100 grs. Alcohol.	Mean.
24°	{ 24.47 23.96	{ 0.1834 0.1771	{ 0.7493 0.7393	0.744 per cent.

At 24.5° the solubility of the plane-symmetrical chloride was 0.7104 per cent. So that if the latter had been formed it would not have been separated from the hexachloride by the recrystallisation, and must have made the percentage of chlorine come out

¹ Ber. d. chem. Gesell. 4, 379.

too low. The dichloride had therefore not been formed (as such), for in the mother-liquors also nothing but hexachloride could be found.

The experiment was now made quantitatively. 5 grams tolane treated exactly as before yielded, after air had been passed through till the weight was constant, 8.9592 grams chlorinated product, or only 0.041 gram less than if the whole had been converted into tetrachloride. On recrystallising I obtained 4.7225 grams hexachloride. This corresponds to 2.968 grams tolane. The remaining 2.032 grams tolane had given, then, 4.2367 ($8.9592 - 4.7225$) grams of the chlorinated product. So that this part of the product contained 52 per cent. of chlorine. It consisted of a red sticky mass in which crystals gradually formed. As no solvent effected a satisfactory separation of the crystals, the chlorine was determined in the mixture just as it was. An exact result was, of course, not to be expected, especially since in the evaporation of the alcoholic filtrates from the hexachloride a volatilisation of 0.233 gram of the substance had taken place. Still the chlorine determination confirmed the result of the above calculation—namely, that besides the hexachloride there had been formed a substance which contained more chlorine than even the tetrachloride.

0.1372 substance gave 0.2675 gram AgCl, corresponding to 47.43 per cent. of chlorine; while the tetrachloride contains only 44.3 per cent.

These experiments prove that in the chlorination of tolane about 60 per cent. of it is converted into "ditolane-hexachloride." There are also formed oily products containing much chlorine.

Now, through the application of my former results to those of Blank we have gained an insight into the constitution of the hexachloride. This view we may in turn apply to the result of the last experiments. For since the hexachloride consists of tetrachloride and plane-symmetrical chloride, the molecules of both these substances must have been formed in the formation of the hexachloride from tolane. And thus the theory is once more confirmed by the proof of the production of the plane-symmetrical chloride.

THE ELECTROMOTIVE FORCE OF METALLIC SALTS.

BY CLARENCE L. SPEYERS.

Owing to the close connection between chemical action and manifestation of electricity, the study of electrical action promises, if it does not solve, at least great assistance towards the solution of the problem, "What is chemical action?" How brilliantly Ostwald's investigations on electrical conductivity of solutions, aided by the dissociation hypothesis of Arrhenius and others, have illuminated chemical phenomena! The darkness surrounding solution,¹ diffusion, electromotive force between solutions of different concentration, thermo-neutrality, etc., has been dissipated. True, the light *may* be false and vanish, but it is the first ever shed on questions hitherto so obscure. If, then, the study of one phase of electrical conduction has taught so much, it is not unreasonable to expect something from an investigation of another side, namely, the separation of electricity or production of an electromotive force.

Ordinary self-continued chemical changes are accompanied by a loss of energy (appearing in the form of heat), and it is natural to suppose that with proper arrangements all this heat can be converted into a corresponding quantity of electricity. In fact, Sir W. Thomson suggested this view. Experience, however, has shown that such a statement does not express the truth; a correction is required which, by some, is supposed to be caused by secondary reactions; by others, with Helmholtz at the head, to be due to the existence of two states of energy, the free and the bound. Applying thermo-dynamics to reversible cells, Helmholtz obtains an expression representing the difference between the chemical (as measured in heat) and the electrical energies consumed and developed respectively in the cell. Experience tells that now the case is correctly stated from a mathematical point of view, but the chemical explanation still remains to be discovered. How this will be achieved is of course at present uncertain, but will it not probably be through the study of the simplest

¹ The writer does not admit that any distinctions are to be made between physical and chemical action other than those of degree and convenience. Of course, mechanical action is excluded.

cases in which an electromotive force is produced? At any rate, it was with this hope that the following investigation was commenced, the plan being to measure the electromotive force of solutions of metallic salts and its variation on systematic dilution. The present paper deals with hydrogen and zinc salts of Cl , NO_3 , $\text{C}_2\text{H}_3\text{O}_2$, and SO_4 .

Instead of zinc, an amalgam of this metal was chosen for two reasons: first, the surface presented to the liquid might be considered as homogeneous; secondly, a tarnishing of the brilliant surface would readily reveal any secondary reaction due to oxidation or hydration. With very few exceptions, whenever the electromotive force had an abnormal value, an examination of the amalgam showed an alteration of the surface, evidenced either by a dull film or loss of mobility. The apparent exceptions were probably due to such a thin film that an alteration of surface could not be perceived but nevertheless existed. The anomalous values were sometimes too high, sometimes too low. Observations were suspended when tarnishing was unmistakably shown. Experiments by Lindeck¹ and others showed that less than 1 per cent. of zinc imparted to mercury an electromotive force equal to that of zinc, justifying the substitution of an amalgam containing 1 per cent. of zinc. Hydrogen amalgam not being available, a zinc amalgam was also used with the acids. The negative electrode was composed of pure mercury, so as to neutralise, as far as possible, any chance alteration of electromotive force due to a change of surface tension.

The mercury was purified by causing it to trickle through a solution of mercurous nitrate, comparative experiments showing that this method was as effective and far more convenient than heating with concentrated sulphuric acid.

All liquids contained one gram equivalent in a liter of water, and, whenever possible, measurements were commenced with solutions of this strength. Zinc chloride and sulphate solutions were prepared by dissolving proper quantities in water, but to obtain solutions of zinc nitrate and acetate, other methods were necessary, owing to the formation of basic salts. The former was successfully made by carefully neutralising normal nitric acid with pure zinc oxide, using tropæolin as an indicator. The latter, by double decomposition between barium acetate and zinc sulphate,

¹ Wied. Ann. 35, 311.

titrating the resulting filtrate with potassium ferrocyanide and diluting with the proper quantity of water. In this way $\frac{1}{2}$ equivalent¹ solution of zinc acetate was easily obtained free from any basic salt.

For measuring the electromotive force a capillary electrometer and compensation cells were used. The method has been so fully described by Ostwald² that anything more would be superfluous. To evaluate the electromotive force between the binding posts of the resistance-box as well as that of the compensation battery, two Clark cells were constructed according to Lord Rayleigh's directions.³ As no difference could be detected when the two cells were opposed, although the electrometer was sensitive to less than 0.0001 V, their electromotive force was considered equal to

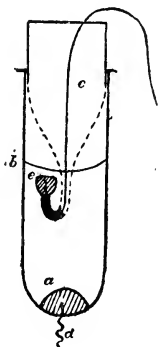


FIG. 1.

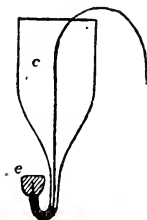


FIG. 2.

1.435 [1 - 0.00077 ($t - 15$)] V. At the close of the present series of experiments a slight inequality (0.001 V) was observable, which, however, could readily be accounted for by a large fluctuation in the temperature of the room during a few cold winter nights, and the Clark cells not having an equal temperature at the time of measurement. Every two weeks the electromotive of the compensation cells was determined, and every day that between the two binding-posts of the resistance-box, the latter being measured by the aid of a compensation cell.

¹ One gram equivalent in two liters of water.

² Zeitschrift f. physikal. Chem. 1, 403.

³ Elementary Pract. Physics, Stewart and Gee, 2, 481.

The cell containing the liquid to be experimented upon is outlined in the two figures. *b* is a portion of a thick test-tube drawn out and a platinum wire fused through the bottom *d*. This tube, with a capacity of about 15 cc., contains the solution and amalgam *a*. Another piece of test-tube is drawn out, a platinum wire inserted and the glass fused around it, at the same time bending the drawn-out portion upward so as to form a cup *e*, in which a globule of mercury can be placed. The platinum wire makes a metallic connection. The piece *c* must be drawn out in such a manner that when the cup is made its orifice is below the surface of the solution contained in *b*. By grinding *c* into *b* a glass stopper is formed, enabling the liquid to be thoroughly mixed after each dilution. Fig. 1 shows *b* and *c* in position; Fig. 2, *c* alone. Four such cells were constructed, enabling duplicate measurements to be made with two solutions at the same time.

The manner of operation was this: Two pipettefuls of the solution were introduced, and then about 0.25 cc. of the carefully cleansed amalgam, the stopper inserted, and the tube gently rocked to and fro, care being taken to fill the cup of the stopper with liquid. The cup was then filled with mercury, which displaced the liquid (the stopper being removed for this purpose), and proper connection made with the electrometer. When the electromotive force became constant, the value was recorded, the mercury in the cup tossed out, the liquid gently shaken, a fresh globule of mercury introduced, and another measurement made. If they did not coincide, the process was repeated until a satisfactory agreement was obtained.¹ Half the liquid being removed, an equal volume of distilled water was added and the above process repeated until the amalgam tarnished. Constant values were often reached in a few minutes with concentrated solutions, but as dilution proceeded a longer interval was required, which in one case (zinc nitrate and sulphuric acid) extended over 60 hours.² Usually, however, 24, but sometimes 12 hours were sufficient for a series. Now and then, the electromotive force would rise and then fall continuously. Under such circumstances the highest value was recorded, justification being found in the fact that no constant value could be obtained by waiting, for the electromotive force decreased continuously throughout a long

¹ In a few cases, noted in the tables, satisfactory results could not be obtained.

² For the completed series.

period of observation. This procedure, however, was only adopted when the highest value of the duplicate was sensibly the same. Such abnormal behavior was observed only with dilute solutions and concentrated acids: caused in the former case, probably, by a slight alteration of the surface of the amalgam; in the latter, by hydrogen evolved from the platinum wire, when the latter was exposed to the strong acid while in contact with the amalgam.

The temperature at which the experiments were made was that of the room, about 20° C.

In the following tables the column headed v contains the number of liters of water in which a gram equivalent of the salt has been dissolved, that headed E. F. the corresponding electromotive force in volts (10° C, G. S.), and that headed Δ the difference between successive values of E. F. Any deviation from the mean exceeding one per cent. is noted in the tables. The observations have all been duplicated and sometimes quadruplicated.

v	$\frac{1}{2}\text{HCl}^1$		$\frac{1}{2}\text{HNO}_3$		$\frac{1}{2}\text{HC}_2\text{H}_3\text{O}_2$		$\frac{1}{2}\text{H}_2\text{SO}_4$		$\frac{1}{2}\text{HCl} + \frac{1}{2}\text{HNO}_3$	
	E. F.	Δ	E. F.	Δ	E. F.	Δ	E. F.	Δ	E. F.	Δ
1	<i>1.1477</i>		<i>1.4335</i>		1.4244		<i>1.4680</i>		<i>1.1540</i>	
2	<i>1.1610</i>		<i>1.4370</i>		1.4417	0.0173	1.4688		<i>1.1683</i>	
4	<i>1.1701</i>		<i>1.4417</i>		1.4415	0.0002-	1.4633	0.0055-	<i>1.1820</i>	
8	1.1903	0.0161	1.4458	0.0102	1.4545	0.0015-	1.4643	0.0010	1.1969	0.0185
16	1.2064	0.0198	1.4560	0.0085-	1.4530	0.0019	1.4649	0.0005-	1.2154	0.0117
32	1.2262	0.0128	1.4475	0.0120	1.4549	0.0024	1.4644	0.0029	1.2271	0.0195
64	1.2390	0.0172	1.4595	0.0008	1.4573	0.0003-	1.4673	0.0035	1.2466	0.0112
128	1.2562	0.0120	1.4603	0.0101	1.4570	0.0030-	1.4708	0.0029	1.2578	0.0100
256	1.2682	0.0118	<i>1.7704</i>	0.0003	1.4540	1.4737	0.0014	1.2758	0.0113
512	1.2800	0.0098	<i>1.4707</i>	1.4751	...	1.2871	0.0101
1024	1.2898	1.2976
		0.0142		0.0041		0.0037		0.0008		0.0143

	$\frac{1}{2}\text{HCl} + \frac{1}{2}\text{HC}_2\text{H}_3\text{O}_2$	$\frac{1}{2}\text{HCl} + \frac{1}{2}\text{H}_2\text{SO}_4$	$\frac{1}{2}\text{HNO}_3 + \frac{1}{2}\text{HC}_2\text{H}_3\text{O}_2$	$\frac{1}{2}\text{HNO}_3 + \frac{1}{2}\text{H}_2\text{SO}_4$ ²	$\frac{1}{2}\text{HC}_2\text{H}_3\text{O}_2 + \frac{1}{2}\text{H}_2\text{SO}_4$
1	<i>1.1402</i>	<i>1.1618</i>	<i>1.4373</i>	<i>1.4485</i>	<i>1.4410</i>
2	<i>1.1630</i>	<i>1.1705</i>	<i>1.4414</i>	<i>1.4490</i>	<i>1.4457</i>
4	<i>1.1750</i>	<i>1.1912</i>	<i>1.4455</i>	<i>1.4507</i>	<i>1.4493</i>
8	1.1933	1.2059	1.4406	1.4518	1.4533
16	1.2120	1.2172	1.4489	1.4501	1.4519
32	1.2269	1.2270	1.4531	1.4544	1.4609
64	1.2305	1.2389	1.4607	1.4620	1.4670
128	1.2565	1.2566	1.4691	1.4603	1.4665
256	1.2678	1.2767	1.4720	1.4637	1.4672
512	1.2868	1.2941	1.4743	1.4584	1.4764

	0.0147	0.0147	0.0041	0.0011	0.0038

¹ The numbers printed in italics are calculated by subtracting once, twice, etc., the mean increment from the first observation. On account of the rapid evolution of hydrogen a stronger acid than $\frac{1}{2}$ th equiv. could not be used.

² Observations varied in some cases about one per cent. from the mean.

v	$\frac{1}{2}\text{ZnCl}_2$.		$\frac{1}{2}\text{Zn}(\text{NO}_3)_2$.		$\frac{1}{2}\text{Zn}(\text{Ac}_2)_2$.		$\frac{1}{2}\text{ZnSO}_4$.		$\frac{1}{2}\text{ZnCl}_2 + \frac{1}{2}\text{Zn}(\text{NO}_3)_2$.	
	E. F.	Δ	E. F.	Δ	E. F.	Δ	E. F.	Δ	E. F.	Δ
1	1.0865		1.3219		1.2598		1.2750		1.0978	
2	1.1060	0.0195	1.3526	0.0307	1.2691		1.2959	0.0209	1.1257	0.0279
4	1.1288	0.0228	1.3713	0.0187	1.2800	0.0109	1.3149	0.0190	1.1467	0.0210
8	1.1570	0.0282	1.3865	0.0152	1.2887	0.0087	1.3357	0.0208	1.1664	0.0197
16	1.1771	0.0201	1.4058	0.0193	1.2887	0.0084	1.3573	0.0247	1.1875	0.0211
32	1.1949	0.0178	1.4263	0.0045	1.2971	1.3604	0.0233	1.2067	0.0192
64	1.4103	0.0160	1.3837	1.2277	0.0210
128	1.2510	0.0233
256	0.0217	0.0174	0.0093	0.0217	0.0219
$\frac{1}{2}\text{ZnCl}_2 + \frac{1}{2}\text{Zn}(\text{Ac}_2)_2$.		$\frac{1}{2}\text{ZnCl}_2 + \frac{1}{2}\text{ZnSO}_4$.		$\frac{1}{2}\text{Zn}(\text{NO}_3)_2 + \frac{1}{2}\text{Zn}(\text{Ac}_2)_2$.		$\frac{1}{2}\text{Zn}(\text{NO}_3)_2 + \frac{1}{2}\text{ZnSO}_4$.		$\frac{1}{2}\text{Zn}(\text{Ac}_2)_2 + \frac{1}{2}\text{ZnSO}_4$.		
1	1.1043		1.0956	0.0208	1.2512		1.2751	0.0282	1.2703	
2	1.1250	0.0208	1.1164	0.0215	1.2689	0.0034	1.3033	0.0261	1.2897	0.0254
4	1.1458	0.0207	1.1379	0.0262	1.2654	0.0558	1.3294	0.0240	1.3151	0.0210
8	1.1665	0.0201	1.1641	0.0212	1.3212	0.0189	1.3534	0.0158	1.3361	0.0128
16	1.1866	0.0202	1.1853	0.0204	1.3401	0.0241	1.3692	0.0248	1.3489	0.0084
32	1.2068	0.0216	1.2057	1.3642	0.0069	1.3940	0.0111	1.3573
64	1.2284	1.3573	1.4051	0.0201
128	1.4252	0.0155
256	0.0207	0.0220	0.0177	1.4407	0.0194
$\frac{1}{2}\text{ZnCl}_2 + \frac{1}{2}\text{HCl}$		$\frac{1}{2}\text{ZnCl}_2 + \frac{1}{2}\text{HNO}_3$.		$\frac{1}{2}\text{ZnCl}_2 + \frac{1}{2}\text{HAc}$.		$\frac{1}{2}\text{ZnCl}_2 + \frac{1}{2}\text{H}_2\text{SO}_4$.				
1	1.0889	0.0269	1.0988	0.0270	1.1088	0.0249	1.1070	0.0291		
2	1.1158	0.0207	1.1258	0.0208	1.1267	0.0220	1.1361	0.0207		
4	1.1365	0.0210	1.1466	0.0159	1.1487	0.0207	1.1568	0.0207		
8	1.1575	0.0211	1.1625	0.0192	1.1694	0.0258	1.1775	0.0204		
16	1.1786	0.0228	1.1817	0.0202	1.1952	0.0230	1.1979	0.0212		
32	1.2014	0.0200	1.2019	0.0221	1.2182	0.0221	1.2191	0.0202		
64	1.2214	0.0224	1.2240	0.0250	1.2403	0.0203	1.2393	0.0211		
128	1.2436	0.0200	1.2490	0.0208	1.2606	0.0241	1.2604	0.0192		
256	1.2636	1.2668	0.0195	1.2847	0.0200	1.2796	0.0173		
512	1.2893	1.3047	0.0239	1.2969		
1024	0.0219	0.0212	1.3278	0.0211		
$\frac{1}{2}\text{Zn}(\text{NO}_3)_2 + \frac{1}{2}\text{HCl}$.		$\frac{1}{2}\text{Zn}(\text{NO}_3)_2 + \frac{1}{2}\text{HNO}_3$.		$\frac{1}{2}\text{Zn}(\text{NO}_3)_2 + \frac{1}{2}\text{HAc}$.		$\frac{1}{2}\text{Zn}(\text{NO}_3)_2 + \frac{1}{2}\text{H}_2\text{SO}_4$.				
1	1.0955	0.0301	1.3581	0.0301	1.3154	0.0300	1.3196	0.0460		
2	1.1256	0.0207	1.3882	0.0161	1.3454	0.0223	1.3656	0.0256		
4	1.1463	0.0197	1.4043	0.0158	1.3677	0.0171	1.3912	0.0226		
8	1.1660	0.0212	1.4201	0.0135	1.3848	0.0129	1.4178	0.0040		
16	1.1872	0.0195	1.4336	0.0026	1.3977	0.0171	1.4218	0.0155		
32	1.2067	0.0206	1.4362	0.0080	1.4148	0.0153	1.4373	0.0027		
64	1.2273	0.0214	1.4442	0.0063	1.4301	0.0004	1.4400	0.0060		
128	1.2487	0.0209	1.4505	0.0019	1.4395	0.0009	1.4460	0.0208		
256	1.2696	0.0198	1.4524	1.4296	1.4668		
512	1.2894		
1024	0.0216	0.0118	0.0163	0.0184		
$\frac{1}{2}\text{ZnAc}_2 + \frac{1}{2}\text{HCl}$.		$\frac{1}{2}\text{ZnAc}_2 + \frac{1}{2}\text{HNO}_3$.		$\frac{1}{2}\text{ZnAc}_2 + \frac{1}{2}\text{HAc}$.		$\frac{1}{2}\text{ZnAc}_2 + \frac{1}{2}\text{H}_2\text{SO}_4$.				
1	1.1013		1.3122		1.3077		1.2957			
2	1.1248	0.0236	1.3282	0.0199	1.3197	0.0083	1.3210	0.0157		
4	1.1484	0.0203	1.3481	0.0319	1.3280	0.0173	1.3267	0.0243		
8	1.1687	0.0214	1.3800	0.0177	1.3459	0.0187	1.3660	0.0212		
16	1.1901	0.0249	1.3977	0.0165	1.3646	0.0105	1.3822	0.0261		
32	1.2150	0.0208	1.4142	0.0160	1.3751	0.0150	1.4083	0.0221		
64	1.2358	0.0208	1.4302	0.0058	1.3901	0.0016	1.4304	0.0245		
128	1.2566	0.0212	1.4244	1.3917	1.4549		
256	1.2778	0.0268		
512	1.3046	0.0317		
1024	1.3363	0.0160	0.0120	0.0223		

¹ Observations varied in some cases about one per cent, from the mean.² Observations varied in some cases about two per cent, from the mean.

<i>v</i>	$\frac{1}{2}\text{ZnSO}_4 + \frac{1}{2}\text{HCl}$		$\frac{1}{2}\text{ZnSO}_4 + \frac{1}{2}\text{HNO}_3$		$\frac{1}{2}\text{ZnSO}_4 + \frac{1}{2}\text{HAc}$		$\frac{1}{2}\text{ZnSO}_4 + \frac{1}{2}\text{H}_2\text{SO}_4$	
	E. F.	Δ	E. F.	Δ	E. F.	Δ	E. F.	Δ
1	1.1039	0.0225	1.2964	0.0213	1.2932	0.0218	1.3228	0.0293
2	1.1264	0.0202	1.3177	0.0270	1.3150	0.0236	1.3521	0.0318
4	1.1466	0.0204	1.3447	0.0231	1.3386	0.0238	1.3839	0.0315
8	1.1670	0.0212	1.3678	0.0296	1.3724	0.0185	1.4154	0.0317
16	1.1882	0.0218	1.3974	0.0154	1.3809	0.0215	1.4471	0.0192
32	1.2100	0.0242	1.4128	0.0352	1.4024	0.0226	1.4603	0.0090
64	1.2342	0.0208	1.4480	0.0090	1.4250	0.0184	1.4753	0.0021
128	1.2550	0.0200	1.4570	0.0054	1.4434	1.4774
256	1.2750	0.0187	1.4624	0.0108
512	1.2937	1.4732
		0.0211		0.0196		0.0215		0.0221

Until more data have been accumulated, the above results cannot be most intelligently discussed, but a glance at the tables will show a few interesting facts.

1. The electromotive force always increases on dilution; the increment of nitric, acetic, and sulphuric acids is very slight, it is true, but still sufficiently marked, in the opinion of the writer, to be unmistakable. At any rate, there is no diminution, and therefore the equivalent electromotive force (electromotive force \times equivalent weight, due account being taken of the quantity contained in the liquid) increases rapidly.

2. Hydrochloric acid has a much lower value than the other three acids, which form a group by themselves, with approximately equal values. It may appear strange that this acid should have an electromotive force so much inferior to that of acetic acid, but the agreement of repeated measurements indicated that they were correct.

3. The electromotive force of a mixture of equal equivalents of an acid with hydrochloric acid is not the mean of the two values, but is only slightly greater than that of hydrochloric acid. The increment also belongs to this acid. Nitric, acetic, and sulphuric acids have an electromotive force so nearly alike that no conclusion can be drawn from their mixtures.

4. Turning to the zinc salts, we find a drop in electromotive force of 33(Cl), 59(NO₃), 166(Ac), and 129(SO₄) millivolts. The first observed values, $\frac{1}{2}$ equivalent, are compared. The increment, however, has been increased. As the solutions are diluted, the fall due to substitution of zinc for hydrogen appears to approach that observed with chlorine, 33 millivolts.

5. Again, the chloride possesses the lowest electromotive force, the other three salts forming a group by themselves, with zinc

nitrate standing out prominently, the latter being caused, in the writer's opinion, by a slight defect in neutralisation, although all care was observed to avoid excess of either constituent.

6. The electromotive force of concentrated mixtures of zinc salts is not the mean of the two values, but only slightly greater than the smaller; zinc acetate and sulphate mixture possibly forming an exception.

7. Turning to mixtures of salts containing the same acid radical but different metals, we find only an approximation to the lower value, and with an increment about equal to that of the zinc salt.

8. Hitherto, chemical action has been excluded, but now consider mixtures of salts and acids having different acid radicals. As might be expected, the electromotive force is only slightly greater than that of the salt having the lower value. It must be remembered that acetic acid is very weak, so that only small quantities of acetates can be formed in the presence of equivalent quantities of the other acids.

9. The electromotive force of $\frac{1}{2}\text{ZnR} + \text{HR}'$ is equal to that of $\frac{1}{2}\text{ZnR}' + \text{HR}$. The agreement is not satisfactory, however, with zinc nitrate and sulphuric acid.

In the next paper it is purposed to describe the results of investigations upon salts of copper.

UNIVERSITY OF MISSOURI, COLUMBIA, MO., *February*, 1890.

THE USE OF ANIMAL CHARCOAL IN THE DETERMINATION OF FAT (ETHER EXTRACT) IN FEEDING STUFFS.

BY H. J. PATTERSON.

The crudeness of the product which goes under the term "ether extract" in fodder analyses is a thing that has impressed itself upon all who have to any extent been engaged in the determination of the various constituents of farm products. How to get rid of a portion, if not all, of this extraneous matter, and have nothing but fat or very closely allied products, has been an interesting question, up to this time unsolved.

To obviate this difficulty I have successfully used animal charcoal, and have obtained a product which in many cases was nearly pure vegetable oil, and in no instance could much foreign matter be detected, getting in every case a product having the general appearance and characteristics of pure fats.

The preparation of the sample and manner of treating the extract has been precisely that adopted by the Association of Official Agricultural Chemists. In filling the percolator tube there was first placed in it the animal charcoal, on top of this a plug of cotton, then the substance to be extracted, and finally another plug of cotton. The cotton serves to make a more uniform stream of ether over the substance, and keeps the latter from crawling up the sides of the percolator.

The plug between the substance and the charcoal will prevent any of the fat coming in contact with the charcoal before it is thoroughly in solution. In a few instances, especially in the case of grains, it was found that the results were a little too low if the fat came in contact with the charcoal before it was thoroughly held in solution by the ether.

In all cases one gram of the substance was used. With grains and meals one gram of charcoal was used, and with hay, fodders, and the like, two grams. The amount of charcoal can be varied at the discretion of the analyst, but the above amounts were found satisfactory. The animal charcoal was a pure article, of medium fineness, thoroughly dried, extracted with ether, and again dried and preserved for use in a well-stoppered bottle. The cotton was of good quality and clean, and had been extracted with ether previous to use.

In the following discussion the method of the Association of Official Agricultural Chemists is designated as Method I, and where charcoal has been employed as Method II.

To prove that there is no loss in passing of pure fat through charcoal, a number of fats were absorbed on cotton and extracted by each of the two methods. The results are given in the following table (A):

TABLE A.

Sample.	METHOD I.			METHOD II.		
	Fat Added. Gram.	Fat Recovered. Gram.	Loss or Gain. Gram.	Fat Added. Gram.	Fat Recovered. Gram.	Loss or Gain. Gram.
Cotton seed oil,	.2180	.2180	0000	.1770	.1760	— .0010
“ “	.2020	.2025	+ .0005	.2015	.2010	— .0005
“ “	.2015	.2010	— .0005	.1815	.1810	— .0005
Average,	.2072	.2072	0000	.1867	.1860	— .0007
Butter,	.1775	.1770	— .0005	.1765	.1760	— .0005
“	.1520	.1510	— .0010	.1880	.1870	— .0010
“	.0910	.0910	0000	.1030	.1035	+ .0005
Average,	.1402	.1397	— .0005	.1558	.1555	— .0003
Mutton tallow,	.1160	.1165	+ .0005	.1470	.1480	+ .0010
“ “	.0960	.0960	0000	.0925	.0930	+ .0005
“ “	.0970	.0970	0000	.0810	.0815	+ .0005
Average,	.1030	.1032	+ .0002	.1068	.1075	+ .0007
Lard,	.0675	.0670	— .0005	.1415	.1420	+ .0005
“	.1345	.1340	— .0005	.0925	.0930	+ .0005
“	.2330	.2325	— .0005	.0660	.0660	0000
Average,	.1450	.1445	— .0005	.1000	.1003	+ .0003
Beef tallow,	.1100	.1100	0000	.1125	.1120	— .0005
“ “	.1515	.1520	+ .0005	.1545	.1540	— .0005
“ “	.0965	.0965	0000	.1335	.1335	0000
Average,	.1193	.1195	+ .0002	.1335	.1332	— .0003
Sum of averages,	.7147	.7141	— .0006	.6828	.6825	— .0003

From this table it will be seen that there is no appreciable loss, and that the two methods are about the same when pure fats are being extracted. The different fats employed give about as much range in composition and physical characters as would be expected in the various vegetable fats.

In Table B is given a comparison of the two methods on a variety of samples, which cover fairly well the different classes of substances met with in agricultural analysis. A comparison of the results given in Table B shows that there is a difference in every case, Method I giving the higher result, and in some cases the difference is surprising. This shows that the amount of error which has been introduced into our valuations of feeding stuffs, calculation of digestibility and nutritive ratios is very much more exaggerated and misleading than has been supposed. The results in Table B are the average of triplicate determinations.

TABLE B.

Description of Sample.	I, Per Cent. Fat.	II, Per Cent. Fat.	Difference Per Cent.
Clover hay,	3.51	2.02	1.49
Corn fodder,	6.17	2.69	3.48
Corn meal,	4.63	4.53	0.10
Cotton seed meal,	10.50	9.88	0.62
Dung from digestion experiment on cotton seed meal,	5.83	3.83	2.00
Oats hay,	4.12	2.57	1.55
Soja bean silage,	5.53	4.70	0.83
Sorghum fodder, "Early Orange,"	5.46	2.70	2.76
Sorghum silage, "Amber,"	6.15	3.68	2.47
Tomatoes (dried),	10.07	6.48	3.59
Unknown pea,	3.44	1.76	1.68
Wheat bran,	3.80	3.33	0.47

Having noticed the acidity of the smell of the extract of some of the samples and of ether which was distilled from the extract of some plants, a few tests of the amount of acid in the extracts, soluble in cold water, were made by titrating it with decinormal sodium hydrate, phenolphthalein being used as an indicator. In nearly every case some acid was found in the extract of Method I, reaching over 1 cc. in some cases, there being scarcely a trace from the extract of Method II. The only case in which there was an appreciable amount of acid in the extract of Method II was from the sorghum silage.

From a study of these figures and a close examination of the products obtained by the two methods, it seems that the use of charcoal results in a closer approximation to the truth than any other method in use, though absolute accuracy is not claimed. The following points may be rightly claimed in favor of the use of animal charcoal in the determination of fat (ether extract) in feeding stuffs.

(1). That the product obtained is nearly pure fat or vegetable oil.

(2). That the product obtained gives a more correct idea of the physical nature of the fats from various substances.

(3). That slight quantities of water that may exist in the substance and pass out with the extract will be removed by the charcoal.

(4). That soluble acids of the plant, or acid which may be formed by the continuous distillation of ether, in connection with some constituents of plants, will be partially, if not wholly, removed by the animal charcoal.

(5). That the animal charcoal will partially obviate, if not wholly remove, the difficulty of change in the amount of ether extract (which generally increases) with the aging of the sample.

MD. AGR'L EXPT. STATION, AGR'L COLLEGE, MD., Feb. 8, 1890.

ON THE SOLUBLE CARBOHYDRATES PRESENT IN THE SEEDS OF LEGUMES.

BY W. MAXWELL.

In the analysis of seeds, all that part of their non-nitrogenous constituents which is soluble in water, and which upon boiling with a dilute acid becomes converted into bodies capable of reducing an alkali-copper solution, has been expressed as dextrine. Prof. R. Sachsse,¹ in a study of *Pisum sativum*, estimated that six and a half per cent. of the soluble nitrogen-free extract matters contained in those seeds was composed of dextrine. He stated, moreover, that not any sugars were present. It has further been decided by A. von Asbóth² that the mature seeds of the various representatives of grain do not contain crystallisable sugars; that in all instances where it had been supposed that cane or glucose sugars were present, the preparations of those bodies which had been obtained were consequent products of the methods employed in research.

Although it may be of small moment, in respect of practical or agricultural considerations, whether the conclusions of the given authorities shall be confirmed or not, there is a special physiological interest in trying to determine more precisely the definite characters of those bodies which comprise the soluble carbohydrate-aggregate of leguminous and other seeds.

In the course of a study of the legumes *Pisum sativum*, *Faba vulgaris*, and *Vicia sativa*, the author³ discovered cane sugar in

¹ Chem. Centralblatt, 1872.

² Bied. Centr., 1888.

³ Landw. Versuchs-Stationen, Bd. 36.

each of those representatives. In addition to saccharose, those examples of seeds contained a white amorphous body which was distinguished chemically from dextrine by the instance that upon boiling with a dilute mineral acid it yielded galactose; and further, when the body was heated with concentrated nitric acid, mucic acid was obtained as the product of oxidation. More recently the seeds of *Phaseolus vulgaris* have been investigated in respect of the presence of soluble carbohydrate bodies, and according to a method and with results which will be more particularised.

The separation of the carbohydrates from the seed material was made by repeatedly extracting with an alcohol of 75 per cent. concentration. The clear extraction was heated to boiling and a saturated solution of strontium hydrate added, and the boiling continued for an hour under a condenser, by which process the carbohydrate bodies were thrown down as saccharates. After some further treatment, the strontium compounds were broken up in aqueous suspension by a current of carbon-dioxide, and the solution evaporated to a syrup. The syrup-residue was extracted by boiling with absolute and 98 per cent. alcohols consecutively, and the extract placed in a desiccator over sulphuric acid. After twenty-four hours a considerable yield of transparent and colorless crystals was obtained, which, upon being recrystallised, appeared in the forms of well-developed monoclinic prisms. The observations of the crystals agreed practically with the crystallographical reading given by Dr. Scholl, Zürich University, of cane-sugar crystals obtained by the author¹ from the seeds of *Faba vulgaris*, and which was as follows:

	Estimated.	Found.
100:110	129°14'	129°9'
110:110	78 36	78 30
100:001	103 17	103 14
001:011	139 30	139 30
011:011	99 0	98 0
110:001	127 31	127 19
111:110	133 59	131 29

After the cane sugar had been separated by extraction with boiling alcohol, a considerable amount of a white-yellow substance was remaining. That residue was taken up in water and

¹ Landw. Versuchs-Stationen, Bd. 36.

treated for the removal of coloring matters, and finally condensed to a very concentrated volume. Upon bringing the solution drop by drop into a beaker containing absolute alcohol, a white, flake-like body separated out, which was brought upon a filter and dried. When the body was boiled with a dilute mineral acid, galactose sugar was obtained, and upon heating with concentrated nitric acid, mucic acid was formed as the oxidation product.

The non-crystallisable carbohydrate which was obtained from the seeds of *Phaseolus vulgaris*, and which was present with some smaller portion of dextrine, seemed to resemble in its appearance and chemical properties the bodies obtained by A. Müntz¹ from *Medicago sativa*, by R. W. Bauer² from *Agar-Agar*, by A. Meyer³ from several caryophyllaceae, by E. Steiger⁴ from *Lupinus luteus*, by A. von Planta⁵ from *Stachia tuberifera*, and by the author⁶ from *Pisum sativum*, *Faba vulgaris*, and *Vicia sativa*, and which are known as "galactans" or "galactins."

No trace of glucoses was observed in the alcoholic extraction, nor in the aqueous solution after the breaking up of the strontium saccharates. It must be remarked, however, that had any reducing sugars been present, they would have been broken up by the treatment with the strontium hydrate.

When the presence of cane sugar, of galactan, with some portion of dextrine, had been established in the seeds treated of, it appeared desirable to make, at least, an approximate estimation of the amounts of those bodies contained. Before such an estimation could be attempted, it was in the first place necessary to determine the conditions by which a maximum extraction of the soluble non-nitrogenous bodies could be effected. As a first experiment, the material was repeatedly extracted with cold water. In another example the material was extracted with water at boiling temperature, and the starch, which was suspended in the extract, was thrown out with a barium solution; that method, however, gave lower results than the extraction with cold water, indicating that some amount of the soluble carbohydrates had been separated either chemically or mechanically with the starch. A third experiment was made by extracting with water at a temperature of 37°-40° C., at which temperature it was observed that a maximum extraction was obtained, and the solution was free from starch,

¹ Compt. rend. **94**.

² J. prakt. Chem. **30**.

³ Ber. d. chem. Ges. **17**.

⁴ Inaugural Dissertation, 1887.

⁵ Landw. Versuchs-Stationen, Bd. **35**.

⁶ Ibid. Bd. **36**.

which was shown by the iodine test. It was determined to extract at 38° C., using water at the same temperature for washing out the residue. The extract solution was treated with a very small volume of phosphotungstic acid, before inverting with hydrochloric acid, the latter being conducted according to Sachsse.¹

The estimations of the inversion products were made gravimetrically as given by Allihn,² and are expressed in the following analytical data:

I. 8.21 grams material yielded = 0.4896 gram sugar.
= 0.440 gram carbohydrates.
= 5.359 per cent.

II. 10.05 grams material gave = 0.599 gram sugar.
= 0.539 gram carbohydrates.
= 5.362 per cent.

The mean of two given weights of material extracted, and of four determinations of the sugar present in the extractions, indicate that the seeds of *Phaseolus vulgaris* contain soluble carbohydrates to the extent of 5.36 per cent.

A quantitative separation of the cane-sugar, galactan, and dextrine was not attempted. A method which would render anything more than qualitative indications of those several bodies does not at present obtain.

When it is known that those soluble carbohydrates are contained in mature seeds, the question occurs most consequently as to what are the physiological uses of those bodies in relation to the life of the embryo-plant during the state of incipient growth? A preliminary observation was made with some material which had been prepared by the direction of Prof. Goodale, Harvard University, for other germination studies.

The seeds of *Phaseolus vulgaris* were germinated and allowed to develop until the radicle was one and a half centimeters in length, at which stage the growth was suddenly stopped by drying the material, seed and radicle together, at 100° C. An estimation of the soluble carbohydrates contained in the material, composed of the partially exhausted seed and the crudely formed radicle, was made exactly the same as in the example of the mature seed.

¹ Chem. Centralblatt, 1877.

² J. prakt. Chem. 22.

- I. 6.865 grams material gave = 0.258 gram sugar.
 = 0.232 gram carbohydrates.
 = 3.37 per cent.
- II. 6.742 grams material gave = 0.262 gram sugar.
 = 0.235 gram carbohydrates.
 = 3.33 per cent.

When the mean of those estimations, 3.35 per cent., is compared with the amount of those bodies contained in the mature seed, it is found that thirty-two per cent. of the soluble carbohydrates had disappeared, were used up by the embryo-plant in the earliest stage of its development, and during the short time which was necessary for the protrusion of the radicle, and before the plumule had made its appearance.

No observation was made in order to determine which of the soluble carbohydrates had first been absorbed by the plantlet. Only so much is indicated by the given experiment that the soluble carbohydrates present in the seed provide the germ with its first requirement of non-nitrogenous substance, and until the starch has been acted upon by the ferments originated by the movement of the germ and prepared for appropriation.

The observations which have been given are preliminary to a proceeding study of the value and disposition of given bodies during germination.

HARVARD COLLEGE LABORATORY.

REVIEWS AND REPORTS.

RECENT PROGRESS IN INDUSTRIAL CHEMISTRY.

III. *Further Notes on the Sulphuric Acid and Alkali Industries.*

Sulphur.—In spite of the nearly complete abandonment of sulphur for acid-making in Europe, the production of the Sicilian deposits has not declined, as is indicated by the following table:

Production and Distribution of Sicilian Sulphur (long tons).

Exported to	1883.	1884.	1885.	1886.	1887.	1888.	1889.
England...	41,788	40,760	33,402	30,236	31,086	37,455	37,633
France...	63,602	65,098	58,264	54,280	56,221	53,927	68,632
Italy.....	66,810	56,292	49,415	48,658	46,818	48,436	44,317
America...	96,629	94,929	99,378	98,590	88,593	128,953	111,838
All other countries.	67,563	56,829	74,123	97,691	89,728	86,590	99,592
Total....	336,392	314,058	314,582	329,455	312,446	355,361	362,012

This country has for many years imported more sulphur than any other; the above table shows that more than one-third of the Sicilian product came to America in 1888. In addition to this, constantly increasing quantities of sulphur are imported into this country from Japan, amounting in 1888 to 6332 tons. Practically no sulphur was mined in the United States in 1888, the deposits at Cove Creek, Utah, not having been worked, although they produced 3000 tons in 1887.

Considerable quantities of sulphur, recovered from tank-waste in England by the Chance process, have been sent to this country during the past year, the importations for 1889 amounting to about 1000 tons. The writer is informed by Mr. George Linder, of Boston, the American agent for the Chance company, that contracts have been made for 500 tons per month during the present year. The Chance sulphur is nearly chemically pure, and commands a higher price than the Sicilian crude; its chief use thus far is in making sulphur dioxide for the sulphite process of wood-pulp manufacture. It would seem particularly well suited for gunpowder making, but has not yet been adopted for this purpose.

The refining of sulphur is still chiefly carried on at Marseilles, where there are now six refineries in operation. These works, with five others at various points in the south of France, produce annually about 60,000 tons of refined sulphur, a very large part of which is used to combat diseases of the vine.

Pyrites.—The Spanish and Portuguese mines are producing pyrites in undiminished quantities. More than two million tons were mined in 1887. The importation of pyrites into England shows no falling off, in spite of the precarious condition of the Leblanc-soda process. According to the Board of Trade returns, the quantity of pyrites imported into the United Kingdom during the past six years is as follows:

Importations of pyrites into the United Kingdom (long tons):

1884.	1885.	1886.	1887.	1888.	1889.
563,073	654,521	556,988	597,595	617,232	643,879

This is practically all supplied by three great companies, the Tharsis and Rio Tinto, in Spain, and Mason & Barry, Portugal. The Rio Tinto Co. made efforts some years ago to introduce Spanish pyrites into France and other countries,¹ and to this end established a large plant for the manufacture of Leblanc soda and treatment of pyrites cinders for silver, gold and copper, at Marseilles. These works are still in operation, but owing to the unpromising outlook of the Leblanc process the project of erecting similar works in Belgium, Austria and America has been abandoned. French pyrites, containing no copper, mined at various points along the course of the Rhone, is employed at all the chief alkali works in France.

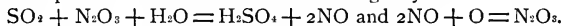
¹ Weldon, J. Soc. Ch. Ind. 1883, p. 4.

In America, the production of pyrites has increased considerably within a few years. In 1888, 54,331 tons of pyrites were mined in the Eastern States, chiefly at the Davis Mines, Franklin Co., Mass. Large quantities of ore are also imported from Canada and Spain. According to W. H. Adams (Manufacturers' Record, Feb., 1890), the mines of Virginia will produce during the present year fully 70,000 tons of pyrites. The same writer estimates the consumption of pyrites for the present year at 250,000 tons. The importations from Canada will probably reach 50,000 tons.

Treatment of Pyrites Residue.—The treatment of the cinders from burnt Spanish pyrites by the Henderson process is carried on in England on an enormous scale, and is constantly increasing. In 1888, 420,415 tons of burnt ore were treated in Great Britain, producing 15,135 tons of copper, 337,500 ounces of silver, and 1918 ounces of gold.

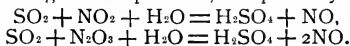
Theory of the Sulphuric Acid Process.—Within the past few years the question of the precise nature of the reactions which take place in the lead-chambers has been fully discussed by Lunge, Raschig, and others, and much light has been thrown on the various stages of the process. An able review of this work has been given by Dr. Hamburger,¹ and need not here be repeated. The chief conclusions reached may, however, be briefly stated.

Lunge,² by a careful study of the gases present in chambers in actual operation, found that nitrogen peroxide (NO_2) is rarely present, and can only exist in practical absence of moisture and sulphur dioxide. Nitrous anhydride, N_2O_3 , is the active agent in the production of sulphuric acid. This view was held by Berzelius, who expressed the reaction in the following way:



Lunge showed that these reactions cannot be correct, since, if true, sulphuric acid whenever formed should be accompanied by a corresponding quantity of nitric oxide; whereas nitrous anhydride only is present in the greater part of the chamber-space. Further, nitric oxide and oxygen do not give nitrous anhydride, as indicated by the second reaction, but yield nitric anhydride or nitric acid according to the absence or presence of water. These observations upset all theories based upon the reduction of nitrogen compounds to nitric oxide. Nevertheless nitric oxide is found to be present to some extent in the first chamber. Lunge considers the material of the "chamber crystals," or nitrosulphonic acid, $\text{SO}_2(\text{OH})\text{NO}_2$, to be an important intermediate product in the synthesis of sulphuric acid. In view of these observations the course of the reaction appears to be as follows:

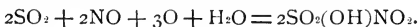
In the first chamber the gases meet in the most concentrated state and at the highest temperature, and probably react thus:



¹ J. Soc. Ch. Ind. 1889, p. 164.

² Chemische Industrie, 1884, p. 5.

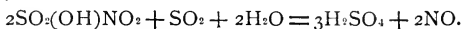
The nitric oxide immediately combines with sulphur dioxide, oxygen and steam to form nitrosulphonic acid :



The nitrosulphonic acid is decomposed by steam :



Or, in the presence of excess of sulphur dioxide and steam, and at a high temperature, the decomposition may take place as follows :



This reaction takes place in the Glover tower, and accounts for the presence of nitric oxide in the first chamber. Lunge explains the loss of nitre in the process by the reduction of part of the nitrogen compounds to lower oxides or free nitrogen, and also the formation of nitrogen peroxide in the last chamber on account of too great excess of nitrous gases and deficiency of sulphur dioxide.

Present Condition of the Alkali Industry.—In spite of the strikingly rapid growth of the ammonia-soda industry, there has been no decline as yet in the production of alkali in Great Britain by the Leblanc process. This is shown by the statistics of the importation of pyrites, given on page 270, and by the following table, compiled from the latest Alkali Inspectors' reports.

Salt decomposed by both processes in the United Kingdom (tons) :

	1884.	1885.	1886.	1887.	1888.
Leblanc process,	578,874	598,096	584,323	577,381	590,312
Ammonia-soda process, .	89,759	115,032	137,220	158,636	212,181
Total, .	668,633	713,128	721,543	736,017	802,493

These figures show that in Great Britain the older process is holding its own, though the world's growing demand for alkali is supplied by the increase of the new industry. Weldon showed five years ago that soda-ash can be produced fully one-third cheaper by the ammonia-soda makers; the survival of the Leblanc process is therefore due to the enormous demand for bleaching powder (which has not yet been made economically by any other method), and to the profits gained in the treatment of pyrites-cinders. Another important gain to the Leblanc industry is the success of the Chance process of sulphur recovery, which has now been introduced into most of the leading alkali works of Great Britain and the Continent. The effect of this new source of profit will be shown in the returns for the present year. The Leblanc-alkali makers have lately devoted themselves almost entirely to the manufacture of caustic soda and soda-crystals, for which the older process possesses important advantages over the new.

Outside of England the advance of the ammonia-soda process has been even greater, while the production of the Leblanc works has fallen off in a marked degree. According to the Paris Exposition Circular of the Solvay Co., the world's total production of alkali in 1888, calculated as soda-ash, may be estimated at about 900,000 tons. Of this amount 430,000 tons, or about one-half, was made by the ammonia-soda process at the various Solvay works. The latter have increased their production still further during the past year, so that it may probably be safely said that more alkali is to-day produced by the ammonia process than by that of Leblanc.

There are now ten Solvay works in operation, the location and output of which are as follows:

Belgium (Couillet),	17,000 tons.
France (Varangeville-Dombasle),	100,000 "
England (Brunner Mond & Co., Northwich),	125,000 "
Germany (Wylhen, Bernburg and Sarralbe),	100,000 "
Russia (Beresniki and Lissitchansk),	17,000 "
United States (Syracuse, N. Y.),	60,000 "
Austria (Ebensee, Salzkammergut),	11,000 "
	<hr/>
	430,000 "

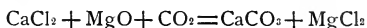
The works at Geddes, near Syracuse, now supply about one-third of the American demand; in addition to the product of these works there was imported from England in 1888 125,135 tons of alkali.

Other modifications of the ammonia-soda process, such as that of Parnell and Simpson (see the writer's second paper on Progress of Industrial Chemistry, this Journal, March, 1889), and the Schloesing process, introduced by Bell Bros., Middlesbrough, England, are worked only on an experimental scale and do not as yet play an important part in the alkali industry.

The Hargreaves Process.—The direct conversion of salt into sulphate of soda by the action of sulphur dioxide and steam has come into increased use during the past few years. There are now five works in England using this process, and also one in Ireland and two in France. During the year 1888 these works produced 43,080 tons of sulphate. The advantages of this method over the ordinary salt-cake process are the avoidance of the cost of making sulphuric acid, and the purity and freedom from iron of the sulphate so obtained. No fuel is found necessary, the heat of the reaction being sufficient after the operation is once started. The disadvantage of the method is the high first cost of the plant. Nearly all the plate-glass now produced in Lancashire is made from Hargreaves sulphate.

Chlorine and Bleaching Powder.—The Weldon Pechiney process, based upon the decomposition of moist magnesium oxy-

chloride by heat into magnesia, hydrochloric acid and free chlorine, is in successful operation at Salindres, France, and has been introduced on a large scale at the works of Albright & Wilson, at Oldbury, near Birmingham, England. An outline of the process was given in the writer's last paper referred to above. This method accomplishes the final conversion into free chlorine of more than 90 per cent. of the hydrochloric acid employed, while the Weldon process, now universally employed, yields only one-third of the chlorine in a free state. An interesting application of the new process has been made at Szczakowa, Galicia, in the manufacture of chlorine from the waste products of the ammonia-soda industry. The residual calcium chloride is converted into magnesium chloride by treatment with magnesia and carbon dioxide,



(as in the last stage of the old Schaffner & Helbig method of sulphur recovery). The magnesium chloride is treated by the Weldon-Pechiney process for the production of chlorine, and the residual magnesia used over again. This method is a partial solution, at least, of the great problem of the production of chlorine from salt in connection with the Solvay process. The great obstacle to the employment of the Weldon-Pechiney process on a large scale is, however, the dilute condition of the chlorine liberated, which makes it unfit for the manufacture of bleaching powder. At present, the method is employed solely for the production of chlorates, for which it is especially adapted. Until the problem of the manufacture of bleaching powder from this weak chlorine is successfully worked out, it is not to be expected that the process will have an important influence on the alkali industry.

Other methods for the production of chlorine from the ammonia-soda residues appear to be unpromising. The Solvays are making hydrochloric acid on a small scale at the Varangeville works, by heating calcium chloride with silica, but the plan makes no progress and is probably very uneconomical. Mond's method of obtaining ammonia and chlorine by passing ammonium chloride vapor over heated nickel or cobalt oxide is still wholly in the experimental stage, though the inventor promises full success in two years at farthest.

Recovery of Sulphur from Tank-Waste.—The Chance process has been introduced at twenty works in Great Britain, one in Austria, and one in France. It was recently stated by the manager of the St. Gobain Co. (France) that the sulphur so regained is sold at a price equal to three times its cost in the form of pyrites. As stated on page 270, considerable quantities of the Chance sulphur are already being exported to America. An important advantage of the process to English alkali makers consists in its availability for the production of either sulphur or

sulphuric acid. If pyrites is cheap, sulphur is manufactured and exported to America and other countries; if pyrites is expensive, the hydrogen sulphide produced from the tank-waste is simply burned to sulphur dioxide and used over again for making acid. It is interesting to reflect that the sulphur imported into England in enormous quantities in the form of pyrites now no longer becomes a source of nuisance in the shape of tank-waste, but passes through the various stages of sulphur dioxide, acid, sulphate of soda, tank-waste and hydrogen sulphide, and finally appears at the end of the process as beautiful crystalline sulphur, a product of high commercial value.

SPENCER B. NEWBURY.

THE USES OF HYDROGEN DIOXIDE IN QUANTITATIVE ANALYSIS, AND THE IMPORTANT METHODS FOR DETERMINING HYDROGEN DIOXIDE.

The more important applications of hydrogen dioxide for quantitative purposes are given below.

Classen and Bauer¹ found that hydrogen dioxide can be used advantageously in the determination of hydrochloric, hydrobromic and hydriodic acids in the presence of sulphuretted hydrogen. The latter is oxidised to sulphuric acid, and the chlorine, bromine and iodine are then determined in the usual manner.

The oxidation of sulphur to sulphuric acid by hydrogen dioxide is also employed to separate arsenic, antimony, zinc, copper and cobalt from the sulphur in their sulphides.

The sulphur can be liberated as sulphuretted hydrogen and oxidised by hydrogen dioxide. They employed this method in the determination of antimony trisulphide, antimony pentasulphide, tin, cadmium, and iron sulphides. It was found that hydrogen dioxide will also readily oxidise sulphur dioxide. This reaction is therefore employed to oxidise barium and sodium sulphites and sodium hyposulphite to sulphates.

P. Ebell² determined lead dioxide by hydrogen dioxide in two ways. He used a known amount of the hydrogen dioxide, allowed it to decompose the lead dioxide, and then titrated the excess with potassium permanganate. He also effected the same decomposition, and measured the volume of the resulting gas. He recommends the former method. The latter method gave results which were too low as compared with those obtained by other methods.

G. Lunge³ described a method for determining potassium permanganate and manganese dioxide by means of an excess of hydrogen dioxide and sulphuric acid. The oxygen evolved was collected and measured, half coming from the manganese dioxide and half from the hydrogen dioxide.

The same author⁴ proposed later a method for determining the

¹ Ber. d. deutsch. chem. Gesell. **16**, 1061.

³ Ber. d. deutsch. chem. Gesell. **18**, 1872.

² Rep. anal. Chem. **6**, 141-43.

⁴ Ibid. **19**, 868.

available chlorine in bleaching powder by means of an excess of hydrogen dioxide, half of the oxygen evolved coming from the bleaching powder and half from the dioxide. But the volume of the oxygen set free is just equal to the total volume of the available chlorine in the bleaching powder.

A. Carnot¹ determined chromic acid by hydrogen dioxide. The slightly acidulated bichromate solution was titrated with very dilute hydrogen dioxide, which was then standardised by means of pure bichromate. The end of the titration is shown by the absence of the blue color when the dioxide is dropped into the chromic acid solution.

G. Lunge² recently recommended the slightly modified nitrometer for standardising potassium permanganate, and for determining bleaching powder and manganese dioxide by hydrogen dioxide and sulphuric acid.

Some of the above decompositions have been employed for the determination of the dioxide itself. These and other important methods for determining hydrogen dioxide will be briefly considered.

Barium dioxide was determined by Brodie³ by treating it with hydrochloric or acetic acid in the presence of finely divided platinum or of animal charcoal, which decomposes the hydrogen dioxide catalytically. The apparatus, including the materials used, was weighed and the acid admitted to the barium dioxide. Decomposition having taken place, the apparatus was again weighed. The loss in weight equals the weight of the oxygen evolved.

In water solution, hydrogen dioxide has been determined by Schönbein.⁴ He acidified the solution with sulphuric acid in order to secure the complete reduction of the permanganate. The solution thus acidified was titrated with standard potassium permanganate until the first traces of color appeared.

Another application of this same reaction has been proposed by F. Hamel.⁵ He treated the dioxide with a permanganate solution, collected and measured the oxygen evolved. At the same time he standardised his permanganate solution for further use.

Instead of potassium permanganate, A. Riche⁶ employed manganese dioxide and sulphuric acid for determining hydrogen dioxide. The oxygen liberated was collected and measured. Lead dioxide is also used for the same purpose.

A method has been proposed by A. Houzeau⁷ which is based on the following reaction in acid solution: $\text{H}_2\text{O}_2 + 2\text{KI} = 2\text{KOH} + 2\text{I}$. A measured amount of standard acid was introduced into the neutral solution of the hydrogen dioxide to be determined. A small excess of potassium iodide was then

¹ Compt. rend. **107**, 948.

² Phil. Trans. 1850. **2**, 779.

³ Compt. rend. **76**, 1023.

⁴ Jour. Soc. Chem. Indst., January, 1890, 21.

⁵ Jour. für prakt. Chem. **79**, 78.

⁶ Jour. pharm. Chim. [6] **13**, 249-56.

⁷ Compt. rend. **66**, 44.

added. The iodine liberated was boiled off and the excess of acid titrated with standard alkali.

Bertrand¹ used the above reaction to determine barium dioxide and hydrogen dioxide. Instead of driving off the iodine and titrating the excess of acid, he titrated the liberated iodine with a standard solution of sodium hyposulphite.

For the detection and determination of small quantities of hydrogen dioxide, Schöne² makes use of the decomposition of potassium iodide by the dioxide in neutral solution, and the detection of the free iodine by means of starch paste. He states that this method will detect 0.00008 gram in a liter. When there is more dioxide present than 0.001 gram in a liter, the method is not accurate, since the color does not change in the same ratio as the substance. A milligram and two-tenths to a liter give about the same color as a gram. The minimum limit of accuracy is 0.00008 gram, and the maximum 0.001 gram of the dioxide to the liter.

G. Lunge³ reversed his method for determining bleaching powder by hydrogen dioxide, and determined the dioxide by means of an excess of bleaching powder. The volume of the oxygen set free was measured, half coming from the bleaching powder, half from the dioxide.

Potassium bichromate has been used by Wilfart⁴ for an approximate determination of hydrogen dioxide. The dioxide was treated with dichromate and sulphuric acid, and the liberated oxygen measured.

A. Carnot⁵ titrated the dioxide with a standard solution of potassium bichromate in the presence of a little hydrochloric or sulphuric acid. Carnot states that this method is not as reliable as the permanganate method.

Attention is called to a piece of apparatus recommended by Maurice de Thierry⁶ for determining hydrogen dioxide.

Some work which I have done in this laboratory shows that the applications of hydrogen dioxide to quantitative analysis can be extended by the use of nitric acid instead of sulphuric. This works more satisfactorily where the formation of insoluble sulphates is involved. Thus, minium and lead peroxide yield thoroughly satisfactory results when treated with nitric acid and hydrogen peroxide. The commercial hydrogen dioxide should in all cases be diluted three or four times to prevent decomposition on standing.

For the determination of minium, an excess of the diluted dioxide and dilute nitric acid are placed in a 200 cc. Erlenmeyer flask. About a gram of minium is weighed in a weighing tube of convenient size, which is then placed upright in the flask. The flask is connected with a Hempel's burette or a Lunge nitrometer.

¹ Bull. Soc. Chim. d. Paris **33**, 148.

² Ber. d. deutsch. chem. Ges. **19**, 868.

³ Compt. rend. **107**, 948.

⁴ Zeit. für anal. Chem. **18**, 154.

⁵ Zeits. für anal. Chem. 1888, 417.

⁶ Jour. pharm. Chim. [5] **12**, 501-2.

The gas volume, after adjustment of pressure, is read. The weighing tube containing the minium is then overturned into the mixture of nitric acid and hydrogen dioxide. In a few minutes the decomposition is complete. The increase in volume is ascertained and reduced to standard conditions of temperature and pressure. Half of the oxygen comes from the minium and half from the hydrogen dioxide. The water in the burette should be made slightly alkaline with sodium or potassium hydroxide, to remove any traces of carbon dioxide which may come from the action of nitric acid on impurities in the minium. The results obtained, expressed in percentages of oxygen, were :

Oxygen.
2.40 per cent.
2.39
2.36

Average, 2.38 +

To test the above results, portions of the same specimen of minium were heated in a vacuum, the oxygen pumped away as rapidly as it was set free, and measured after removal of carbon dioxide. Under these conditions the minium passed completely into lead oxide. The results were :

Oxygen.
2.37 per cent.
2.36
2.36

Average, 2.36 +

We attempted to determine the oxygen in the same specimen of minium by heating it in hard glass tubes attached to a Hempel's burette and measuring the oxygen evolved. Platinum gauze was placed in the tube to facilitate the distribution of heat. The results, expressed in percentages of oxygen, were :

Oxygen.
2.19 per cent.
2.21
2.22
2.26
2.20

Average, 2.21 +

As will be seen, the results are too low. This is to be attributed to a partial recombination of the lead oxide and oxygen during cooling.

The method¹ sometimes employed for determining lead dioxide

¹ Zeits. für anal. Chem. **14**, 348.

by heating in the air and ascertaining the loss in weight is subject to the same source of error.

The determination of lead dioxide was carried out in all respects like that of minium. The specimen should be finely pulverised, and a half gram or less used in a determination. The results with hydrogen peroxide and nitric acid, expressed in percentages of oxygen evolved, were:

	Oxygen.
	5.43 per cent.
	5.43
	5.42
	<hr/>
Average,	5.42 +

Determinations of the same specimen by heating in a vacuum were carried out as in the former case. More carbon dioxide was found here than in the minium. .3 per cent. of carbon dioxide was removed from the oxygen. The results, expressed in percentages of oxygen, were:

	Oxygen.
	5.45 per cent.
	5.43
	<hr/>
Average,	5.44

The determination of manganese dioxide by hydrogen dioxide and sulphuric acid has been made by Lunge as above mentioned. But we find that nitric acid is preferable, as will appear below.

A specimen of manganese dioxide was ground and dried. Two determinations were made by Lunge's method, with the following results:

	Oxygen.
	13.13 per cent.
	13.14
	<hr/>
Average,	13.13 +

Two determinations of oxygen in the same specimen, made with the use of dilute nitric instead of sulphuric acid, gave:

	Oxygen.
	13.17 per cent.
	13.24
	<hr/>
Average,	13.20 +

The slightly higher results in the second case are perhaps due to the presence of ferrous iron in the ore, which was oxidised by the nitric acid, and loss in available oxygen avoided. To test this we added equal amounts of a ferrous salt to weighed portions of the manganese dioxide, and determined the oxygen by sulphuric and nitric acids respectively. The results obtained when sulphuric

acid was used were slightly lower, while when nitric acid was employed they were practically constant. This tends to confirm the above idea.

That hydrogen dioxide can be determined by minium and nitric acid, or lead dioxide and nitric acid, will be seen from the following results. The specimen was first determined by calcium hypochlorite. The results are expressed in liters of oxygen obtained from one liter of hydrogen dioxide.

Results when calcium hypochlorite was used :

	Oxygen.
	5.890
	5.890
	5.880
	<hr/>
Average,	5.8866 +

Results when minium and nitric acid were employed :

	Oxygen.
	5.900
	5.910
	5.910
	<hr/>
Average,	5.9066 +

Results from the decomposition by means of lead dioxide and nitric acid :

	Oxygen.
	5.910
	5.900
	5.910
	<hr/>
Average,	5.9066 +

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

H. C. JONES.

A DICTIONARY OF APPLIED CHEMISTRY. By T. E. THORPE, B. Sc. (Vict.), Ph. D., F. R. S., assisted by eminent contributors. In three volumes. Vol. 1. London and New York: Longmans, Green & Co., 1890. Price of Vol. 1, \$15.00.

The following extract from the preface of this work will explain its object :

"This work is essentially a dictionary of chemistry in its applications to the arts and manufactures; hence it deals but sparingly with the purely scientific aspects of chemistry, unless these have some direct and immediate bearing upon the business of the technologist. For all such matters reference is made to the new edition of 'Watts' Dictionary of Chemistry,' by Dr. Forster Morley and Mr. Pattison Muir, to which, indeed, the present work

may be said to be complementary. In order to facilitate such reference the general plan and method of arrangement of the two dictionaries are similar, and the nomenclature and notation adopted are practically identical." "Although the two works are, in a broad general sense, complementary, it is practically impossible to avoid a certain amount of overlapping, and therefore a certain degree of independence. Hence in the present work the chemical history of a product of technical importance, so far as it is known, has often been completed, although its derivatives have, at present, no applications in the arts. Moreover, such subjects as the atmosphere, water, fermentation, the chemistry of the hydrocarbons, the vegeto-alkaloids, glucosides, etc., etc., all of which are dealt with in the other work, find also a place in this dictionary by reason of their relations to technology or to medicine and sanitation. In all cases, however, these subjects are treated from the standpoint of practical application."

The first volume ends with *Dysodil*. Among the longer and more important articles contained in it are: *Disinfectants*, by A. H. Allen; *Copper*, by E. J. Ball; *Butter*, by James Bell; *Acidimetry and Alkalimetry and Analysis*, by C. H. Bothamley; *Cellulose*, by C. F. Cross; *Balance and Cyanides*, by W. Dittmar; *Candles*, by Leopold Field; *Aniline, Aniline Black, Aniline Blue, Aniline Salt, Benzene and its Homologues*, by R. J. Friswell; *Anti-corrosive Compositions and Methods, and Anti-fouling Compositions*, by J. B. Hanway; *Cements*, by W. N. Hartley; *Brewing*, by John Heron; *Bleaching, Dyeing, Detection of Colors in Dyed Fabrics*, by J. J. Hummel; *Benzaldehyde, Benzoic Acid, Cinnamic Acid, Cymenes, Diphenyl, etc.*, by F. R. Japp; *Ammonia, Bromine, and Chlorine*, by G. Lunge; *Azo-coloring Matters*, by Raphael Meldola; *Animal Charcoal*, by J. A. R. and B. E. R. Newlands; *Creosote*, by B. Nickels; *Alizarin and Allied Coloring Matters*, by W. H. Perkin, Jun.; *Alloys and Assaying*, by W. C. Roberts-Austen; *Albuminoids*, by H. H. Robinson; *Agate, Corundum, Diamond, etc.*, by F. W. Rudler; *Balsams, Camphor, Chloroform, etc.*, by Alfred Senier; *Carbohydrates*, by Cornelius O'Sullivan; *Alcohol*, by G. N. Stoker; *Barium, Calcium*, by A. E. Tutton; *Cereals, Citric Acid*, by R. Warington; *Azines*, by Otto N. Witt; *Aurine*, by W. P. Wynne; *Distillation*, by Sydney Young.

It is evident from this list that the editor has selected his contributors with care, and that, so far as possible, the articles have been written by men who are specially fitted to write on the subjects assigned to them. We may fairly assume that Professor Lunge gives us reliable information on the subjects of ammonia and bromine and chlorine; and the same may be said of Professor Roberts-Austen and Assaying, Professor Meldola and Azo-coloring Matters, Dr. Witt and Azines, etc. It would almost be an impertinence to question their statements.

As examples of thoroughness and clearness the articles on Analysis, Bleaching, Brewing, Carbon, Cellulose, Cement, Chlorine, Cyanides, Disinfectants, Distillation, and Dyeing are worthy of special mention.

The chemist, whether engaged in technical work or not, will find the book of great value, and he will hardly look for information without finding it. There is, in fact, no other book in English or in any other language which gives as fresh and as reliable information on subjects connected with industrial chemistry.

NOTES.

The Chemical Examination of Baking Powders.

Bulletin No. 13 from the Chemical Division of the U. S. Agricultural Department discusses the results of recent investigations into the composition and relative values of the common baking powders.

Nothing has been invented which equals the action of yeast for aeration of bread, since it introduces no foreign materials, but makes the required carbon dioxide from the carbohydrates already existing in the dough. Another method which leaves no residues in the bread is that invented by Dr. Dauglish, in which the dough is worked under pressure with water charged to saturation with carbon dioxide. On relieving the pressure the dough rises at once. This method has the advantage of being speedy, but bread so made is rather insipid. It is used to some extent in the larger cities of Great Britain.

The demand for a quick-rising dough has been met in this country by the various forms of baking powder, and their use has grown to very large proportions. It is estimated that from fifty to seventy-five millions of pounds are consumed annually in the United States, the smaller number representing a value of twenty-five millions of dollars. Many suppose that all the constituents of the powders are driven off in the process of baking, and this opinion is encouraged by the manufacturers; it is, of course, untrue in nearly all cases, and the character of the residues, in view of the enormous consumption of bread containing them, becomes of very great importance.

Baking powders consist essentially of a carbonate or bicarbonate to supply the carbonic acid gas, and an acid which can liberate it, together with some inert substance, usually starch, to prevent chemical action on standing, due to too close contact of the active

ingredients and too rapid evolution of gas when the powder is used. The different powders in use may be conveniently classified as follows by their acid constituents, bicarbonate of soda being almost universally employed as the alkaline ingredient :

(1) *Tartrate powders*, in which the acid part is taken by tartaric acid or, more commonly, its acid potassium salt. Of this class the report says, "the residue is probably the least objectionable of any of those left by baking powders." This residue is simply potassium-sodium tartrate or Rochelle salt. The amount contained in a loaf of bread made with tartrate powder is about equal to the quantity contained in a Seidlitz powder. Free tartaric acid leaves less residue, but it is more difficult to regulate the evolution of gas when the powders are made from it, and they are more likely to deteriorate on standing.

(2) *Phosphate powders*. Monocalcium phosphate is here employed to liberate the carbon dioxide. It is made by the action of sulphuric acid on bone, and nearly always contains some calcium sulphate as impurity. The residues from the phosphate powders consist of the insoluble phosphates of calcium and sodium. It may be said in general that these residues are not more objectionable, though larger in quantity, than those from the tartrate powders.

(3) *Alum powders*. The gas is set free by the action of either potassium or ammonium alum, no distinction being made commercially between the two. The residues from such powders contain hydrate of aluminum, sodium sulphate, and either potassium or ammonium sulphate, according to the alum employed; very commonly both are present. There is considerable doubt as to the effect of the ammonium salt on the human system. Professor Cornwall, of New Jersey, calls attention to the irritating effects of various other ammonium salts, and thinks careful examination of the action of the sulphate is urgently needed. Tartaric acid or acid calcium phosphate is often added to alum powders with the intention of causing more rapid evolution of gas at first. The former mixture is objectionable, as the aluminum is liable to be retained in soluble form, as the tartrate, instead of being changed to the insoluble hydrate. The mixture of the acid phosphate with the alum powder, on the other hand, is an improvement, since aluminum phosphate is still less soluble than the hydrate. The "alum question" has been much discussed, and, from all the evidence obtainable, the following conclusions are drawn :

(a) That form of alum powder in which sufficient phosphate is added to combine with all the aluminum present is a better form, and less apt to bring alum into the system than where alum alone is used.

(b) It must be expected that small quantities, at least, of alum will be absorbed by the digestive fluids when any form of powder containing it is used.

(c) Whether the absorption of small quantities of alum into the human system would be productive of serious effects is still an open question, and one that careful physiological experiment alone can decide.

In general, it may be said that of the three classes of powders, a tartrate powder gives the lowest percentage of carbon dioxide in proportion to the weight of chemicals used, together with least weight of residue; and a straight alum powder gives the highest proportion of gas and greatest weight of residue.

Ammonium carbonate is sometimes used as a baking powder. Being volatile at baking temperature, no acid is required. If there were certainty of driving off all of it in baking there could be no objection to its use; but, since it acts as a corrosive poison when taken in considerable quantities, great care should be exercised when it is employed.

The report suggests that with a little care baking powders could be made at home at much less cost than the market price. It recommends as a permanent powder, easily made and without specially drying the ingredients, the following proportions, intimately mixed:

Cream of tartar,	8 oz.
Baking soda,	4 "
Corn starch,	4 "

If too little starch is used, baking powders deteriorate when kept; if too much, the powder is weakened.

Curiously enough, no such thing is recognized in legislation as adulteration of baking powder unless some substance is included which can be shown to be injurious to health. Merchants can be prosecuted for selling impure cream of tartar, but if it is mixed with other chemicals and sold as baking powder no law is violated. Yet it can hardly be denied that some safeguard is needed with a substance so widely and so constantly used. The report recommends that manufacturers be required to use a label giving approximately the composition of the powder sold. "This is in harmony also with modern ideas in regard to legal regulation of the sale of food-stuffs, the tendency nowadays being to allow the sale of cheap substitutes for any article of food so long as they are not injurious to health, but to make all possible provision to insure that the purchaser shall know exactly what he is getting." Attention may be called to analogous regulations concerning fertilizers, and it is shown that all reasons for such requirements in this case apply with equal or greater force when applied to the subject of baking powders.

J. H. HOLMES.

Perseite, a Heptacid Alcohol.

M. Maquenne has recently made known¹ the results of his investigation of the subject of the composition of perseite, a sub-

¹ Ann. chim. Phys. [6] 19, 5 (January, 1890).

stance found in the leaves, berries, etc., of the *Laurus Persea*. Discovered in 1831 by Avequin, who supposed it identical with mannite, as did also Melsens, who made the first analysis of the substance, perseite was regarded by Müntz and Mercano¹ as *isomeric* with mannite, having, however, a higher melting point, possessing no rotatory power, and differing markedly also from that alcohol in crystalline form. From dulcite, which melts at the same temperature, it is to be distinguished by its lesser crystallising power, and by the fact that, like mannite, its aqueous solution becomes dextro-rotatory on addition of borax. Perseite is very soluble in hot water; on cooling, the solution deposits the greater part of the substance in crystalline condition. It is almost insoluble in alcohol.

M. Maquenne now finds that perseite is not isomeric with mannite, but is a *heptacid* alcohol derived from heptane. A mere determination of the percentage of carbon and hydrogen in perseite would not be likely to lead to any satisfactory conclusion with regard to the composition of the substance, since the percentages of carbon in compounds represented by the formulae $C_6H_8(OH)_6$ and $C_7H_9(OH)_7$ differ by only six-hundredths; of oxygen by but eight-hundredths of one per cent. Even in the proportions of hydrogen the difference amounts to only fifteen-hundredths of one per cent. A careful study, therefore, of several derivatives was necessary in order to establish the composition of this alcohol. It should be mentioned in passing that a determination of the molecular weight by Raoult's method did not yield satisfactory results.

In the presence of zinc chloride, acetic acid and perseite react upon each other, giving rise to the formation of a heptacetate, $C_7H_9(O.CO.CH_3)_7$. The analysis of this compound gave figures agreeing almost exactly with those required for a substance of the formula given above, and, further, by saponification by means of baryta and determination of the barium acetate formed, the proportion of acetic acid in the heptacetate was shown to be that expressed by the formula. A heptabutyrate, $C_7H_9(O.CO.C_4H_7)_7$, was also made and analysed by the same methods. Fuming nitric acid forms with perseite a heptanitate, $C_7H_9(NO_2)_7$, which resembles nitromannite and nitroinosite, but is more stable. A compound with benzoic aldehyde was prepared and shown to have the composition expressed by the formula $C_7H_{12}O_7(CH.C_6H_5)_2$, where four hydrogen atoms belonging to the alcoholic hydroxyl groups are replaced by the two bivalent groups $(CH.C_6H_5)$.

By heating with hydriodic acid, perseite is converted chiefly into two products: a hydrocarbon of the formula C_7H_{12} , and an iodide of heptane, $C_7H_{15}I$. The hydrocarbon was carefully examined and was found to possess none of the characteristic properties of the hydrocarbons of the acetylene series or of the di-ethylene

¹ Ann. chim. Phys. [6] 3, 279 (1884).

series. It does not combine with the halogens or with the halogen acids to form corresponding derivatives of heptane; the molecule is bivalent, and the products of the action of these reagents are substances whose composition is represented by the formulae $C_7H_{13}Cl$, $C_7H_{13}I$, $C_7H_{12}ClBr$, $C_7H_{12}Br_2$. The derivatives and the hydrocarbon itself show a strong tendency to polymerise. These observations led M. Maquenne to the conclusion that the hydrocarbon must be related to the terpenes, and, indeed, he was able to extract from turpentine a "heptene" which proved to be identical with that formed from perseite. Finally, there was nothing in the reactions of perseite to lead one to the conclusion that the substance is either an aldehyde or a ketone.

W. W. RANDALL.

*Density, Color and Spectrum of Fluorine.*¹

In these new experiments on fluorine, Moissan has prepared the gas in much larger quantity and in a greater state of purity, and has determined some of its physical constants. The method of preparation is identical with that already described,² the apparatus being somewhat larger and the amount of hydrofluoric acid decomposed being greater. The method of purification consisted in passing the fluorine evolved through a platinum spiral cooled down to -50° in a bath of methyl chloride, and then over fragments of sodium fluoride contained in platinum tubes. By this method fluorine entirely free from hydrofluoric acid was obtained. By means of a special platinum flask resembling those used by Berthelot to determine specific heat of liquids and by Charcel to determine density, Moissan found the density of fluorine to be 1.265, the theoretical density being a little higher, viz. 1.316.

Fluorine, on account of its properties and atomic weight, belongs naturally at the head of the chlorine family of elements (F, Cl, Br and I). As all the elements of this family in the gaseous state are colored, and, moreover, the intensity of the color diminishes gradually from iodine to chlorine, it was important to determine whether fluorine possesses any special color. In the previous paper fluorine has been described as a colorless gas, and when thin layers are looked at it apparently has no color. When, however, the gas is inclosed in platinum tubes from a half to a meter in length and closed by plates of transparent fluorspar, a decided color is noticed when a white background is looked at. With a depth of half a meter fluorine is plainly seen to possess a greenish-yellow color, much fainter than that of chlorine seen under the same depth, and, moreover, differing from chlorine in that the shade approaches more towards yellow. Examined by means of the spectroscope under a depth of a meter, fluorine does not show any absorption bands.

¹ C. R. 109, 861; 937.

² This Journal 8, 445.

When a small quantity of water is introduced into the platinum tube the water is decomposed, giving hydrofluoric acid and ozone. This last gas is produced in such a state of concentration that the whole tube takes a deep indigo-blue tint. After a few minutes, owing to the temperature of the laboratory, the ozone is destroyed, the blue tint becomes fainter and fainter and finally colorless. This is the first experiment in which ozone has been produced so concentrated at ordinary temperatures.

The spectrum of gaseous fluorine was determined by Moissan to consist of thirteen lines in the red portion of the spectrum. Five of these agree very well with those already determined by Salet, by comparing the spectra of the chloride and fluoride of silicon.

W. R. ORNDORFF.

Celebration of the Twenty-fifth Anniversary of Kekulé's Benzene Theory.¹

The German Chemical Society arranged a banquet on the 11th of March in honor of Prof. August Kekulé, it being twenty-five years since Kekulé published his theory of the structure of benzene. Beside the chemists resident in Berlin, many other guests were present, including some of the most noted chemists in Germany, those prominent in industrial chemistry as well as those known as teachers; foreign chemical societies, the German government, and the city of Berlin sending representatives.

Before the dinner there was a meeting in the hall of the Rathaus. The president of the society, Prof. A. W. v. Hofmann, greeted the guests in an interesting speech; he noted that this was not the first time chemical discovery had been thus celebrated; he recalled the 100th anniversary of the discovery of oxygen by Priestley, celebrated in America in 1874, and the 50th anniversary of Wöhler's synthesis of urea, celebrated at Göttingen in 1878. It was a feature of the banquet to-day that the man whose theories they celebrated was present and could hear of the importance to which his theory had helped to raise chemical industry. The speaker referred to the time when illuminating gas compressed in iron cylinders was brought to the houses of the consumers, and it was found that the gas partly lost its illuminating power by standing in the cylinders. Faraday showed in 1825 that this was owing to the separation of a liquid—benzene—from the gas. The speaker showed the guests a sealed glass tube containing a few drops of benzene, which Faraday had given him with the advice to keep this very volatile liquid sealed up to prevent evaporation. No one could have foreseen that after a few decades the same liquid would be isolated in quantities of millions of kilograms.

Prof. v. Hofmann closed by introducing Kekulé's oldest pupil, Prof. A. v. Baeyer.

¹ Prepared by E. Renouf from an account given in the *Chemiker-Zeitung* for March 15th, 1890.

Prof. v. Baeyer took as subject for his remarks Kekulé's benzene theory. He showed how the brilliant theories of Kekulé step by step had opened the path to our present views of the structure of chemical compounds; the foundations for the new views were given by his paper on the tetravalence of carbon, published in 1858, and by the illustrative model which he used, representing the atom of carbon as a black ball in the center of a tetrahedron, and to represent its power of union, four rods reaching from the black ball to the points of the tetrahedron, the rods ending in four white balls representing atoms of hydrogen. The paper on the benzene theory was published January 27th, 1865, in the *Journal of the Société de Chimie at Paris*, and on the 26th of February appeared in German in Liebig's *Annalen*. The speaker discussed the opposing theories of the structure of benzene, brought up the objections to the prism theory and to the diagonal nucleus, and claimed that the clearest expression of the structure of aromatic compounds was still Kekulé's benzene ring. Doubtless science would not remain content with this, but would strive to build the structure further; but the point of special significance for the celebration of the day was that the theories of Kekulé had for twenty-five years stood the test of time, and to-day still pointed out the direction of further labor on the building of the structure theory.

Speakers from foreign societies and from the chemical industry followed; then Kekulé spoke, thanking for the honors shown him. Referring to his early studies, he said his father had trained him as an architect, and that he had drawn and planned industriously till he took up the study of chemistry.

Two circumstances had helped him in building up his theories: first, that as a pupil of Dalton and of Liebig, and indeed of all the great chemists of the time, he had belonged to no one special chemical school of thought; and, second, that as a consequence of his architectural training he always strove in his thoughts for a material representation of his ideas of structure. While in London, his mind filled with these subjects, the picture of the union of the atoms in benzene appeared to him in a dream, and on waking he jotted down the principal points of the structure theory, which he then carefully studied and worked out, publishing it eight months later.

After three cheers for Kekulé the guests then went to the dinner at the Hotel Kaiserhof.

AMERICAN CHEMICAL JOURNAL.

Contributions from the Chemical Laboratory of Harvard College.

LXVIII.—ON TETRABROMDINITROBENZOL.

BY C. LORING JACKSON AND W. D. BANCROFT.¹

After it had been determined that the tribromdinitrobenzol, melting at 192° , reacted easily with a variety of substances, it seemed of interest to try similar experiments with a tetrabrom compound, and we selected for this purpose the tetrabromdinitrobenzol, melting at 228° , and describe in this paper the results of our work, which may be briefly summarised as follows. Tetrabromdinitrobenzol is not acted on by alcoholic ammonia in open vessels, but, if heated with it in a sealed tube, is converted into a yellow substance insoluble in all the common solvents, which seems to be the bromtriamidodinitrobenzol. With aniline the bromtrianilidodinitrobenzol, melting at 175° – 176° , is formed. With sodium malonic ester it gives in the cold dibromdinitrophenylmalonic ester, melting point 89° , which possesses acid properties, forming a red sodium salt, and is converted by aniline into the bromanilidodinitrophenylmalonic ester, melting at 127° . The action of these reagents on the tetrabromdinitrobenzol is therefore similar to their behavior with tribromdinitrobenzol, the fourth atom of bromine remaining unaffected in all these reactions. We were prevented by want of time from trying to remove this fourth atom of bromine by reactions carried on at higher

¹ Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

temperatures. We have studied also the reduction of the dibrom-dinitrophenylmalonic ester with tin and hydrochloric acid, and have obtained in this way the bromamidooxindol, $C_6H_2BrNH_2(CH_2CONH)$, melting at about 212° , and its chloride, $C_6H_2BrNH_2(CH_2CONH)HClH_2O$. We may add, that in preparing the tetrabromdinitrobenzol from somewhat impure tetrabrombenzol we obtained the as yet undescribed pentabromnitrobenzol, which melts at 248° , and on another occasion the hexabrombenzol.

Preparation of Tetrabromdinitrobenzol.

Our starting point in the manufacture of the tetrabrombenzol was tribromaniline, which we prepared as follows. 60 grams of aniline were dissolved in dilute hydrochloric acid, and the solution having been made up to a volume of about three liters, a rapid stream of air saturated with bromine vapor was sucked through it by means of a Bunsen pump until the liquid assumed a distinct yellow color. The precipitate of tribromaniline was then removed by straining through cheese-cloth, washed with a stream of common water until free from acid, when the greater part of the water was squeezed out with a screw press and the product thoroughly dried on a steam radiator. In this way a quantitative yield of tribromaniline free from colored by-products was obtained at a much less expense of time and labor than by the method formerly in use.

To convert the tribromaniline into tetrabrombenzol we used the method of V. von Richter¹ slightly modified, which left nothing to be desired so far as the yield was concerned, when the process was successful; this, however, was not always the case, as frequently the product was a substance melting in the neighborhood of 87° , from which tetrabrombenzol melting at 98° could be obtained only by repeated crystallisation from a mixture of alcohol and benzol, and even then not in large quantity.² In spite of many experiments, we have not succeeded in determining with certainty the conditions under which this mixture was formed, or the nature of the impurity which it contained, and can give only the conditions which usually gave a good result. 25 grams of the

¹ Ber. d. chem. Gesell. 8, 1428.

² Owing to this uncertainty in our modification of Von Richter's process, we made two attempts to use Sandmeyer's method, but encountered such difficulties in applying it to tribromaniline that we decided it was easier to prepare our material by Von Richter's process than to overcome these difficulties.

tribromaniline were dissolved in a small quantity of glacial acetic acid with the aid of heat, and, after the solution had cooled, a concentrated aqueous solution of hydrobromic acid¹ was added, which threw down a precipitate of tribromaniline bromide; the mixture was stirred vigorously, and, disregarding the precipitate, a concentrated aqueous solution of about the theoretical amount of sodic nitrite added in small portions, keeping the solution cool by immersing the beaker containing it in cold water; the beaker was then warmed gently on the water-bath, and solid sodic nitrite added in small pieces until the proportion of the total sodic nitrite to the tribromaniline was three molecules to one (this very large excess of sodic nitrite being found necessary to complete the reaction). The liquid on cooling deposited a tarry mass, which was extracted repeatedly with small quantities of hot alcohol until it was converted into crystals (melting at about 95°). An additional amount of these crystals was obtained by pouring into water the red liquid from which the tar had been deposited, but this amount was not large. The product, after purification by one or two crystallisations from hot alcohol, showed a yield of from 89 to 93 per cent. of the theoretical.

To convert the tetrabrombenzol into tetrabromdinitrobenzol, 10 grams of it were dissolved with the aid of heat in nitric acid of specific gravity 1.52, prepared in the laboratory from nitre and sulphuric acid; then the same volume of strong sulphuric acid was added, about 200 cc. of the mixture of the two acids being used, and, after standing in the cold for ten minutes, the whole was boiled for about an hour in a flask closed with a glass bulb. If the tetrabrombenzol was sufficiently pure there was little foaming and no violent action, and on cooling a white crystalline solid separated, which was nearly pure tetrabromdinitrobenzol, and, after crystallisation from benzol with a little alcohol, or from chloroform, showed the right melting point 228°.²

¹ An attempt to substitute potassic bromide and sulphuric acid for hydrobromic acid gave a much poorer yield; less than 50 per cent. instead of 90.

² One of us and J. F. Wing (this Journal **10**, 291 (1883), some years ago obtained tetrabromdinitrobenzol as a secondary product in the manufacture of tribromtrinitrobenzol, but we were unable to raise its melting point above 224°; this was ascribed at the time to the presence of a little tribromtri- (or di-) nitrobenzol, an opinion which is confirmed by the fact mentioned above that tetrabromdinitrobenzol prepared by us according to the usual method showed the melting point 228° given by Von Richter (Ber. d. chem. Gesell. 1875, p. 1427). The difficulty in removing the tribrom compound can be accounted for by supposing that it forms the addition-product observed by one of us and G. D. Moore (Ber. d. chem. Gesell. 1888, p. 1707), or an analogous one with the trinitro compound.

If, on the other hand, a tetrabrombenzol was used containing some of the impurity already mentioned, which, when present in quantity, lowered the melting point to the neighborhood of 87° , the action was violent, the boiling being accompanied by much foaming, the product was often oily, and, after most of the solid had been precipitated by water, the aqueous liquid contained decomposition-products, as was shown by the blackish precipitate formed in it on the addition of sodic carbonate. The main product in this case was a mixture of the tetrabromdinitrobenzol and another substance, which was obtained by treatment with aniline or sodium malonic ester, and subsequent separation of the derivative of the tetrabromdinitrobenzol by crystallisation out of alcohol from the unaltered second product, which was then purified by crystallisation from boiling alcohol, or better, chloroform, until it showed the constant melting point 248° , when, after drying at 100° , it was analysed with the following results:

I. 0.1711 gram of the substance gave on combustion 0.0855 gram of carbonic dioxide and 0.0151 gram of water.

II. 0.2100 gram of the substance gave 0.1075 gram of carbonic dioxide and 0.0103 gram of water.

III. 0.1846 gram of the substance gave 3.5 cc. of nitrogen at a temperature of 17° and a pressure of 773 mm.

IV. 0.1881 gram of the substance gave, according to the method of Carius, 0.3418 gram of argentic bromide.

	Calculated for $C_6Br_5NO_2$.	I.	II. Found.	III.	IV.
Carbon	13.90	13.63	13.96
Hydrogen	0.00	0.98	0.54
Nitrogen	2.70	2.24	...
Bromine	77.23	77.34

There can be no doubt, therefore, that this is the as yet undescribed pentabromnitrobenzol.

Properties.—The pentabromnitrobenzol crystallises in very slender little white needles which melt at 248° . The substance is essentially insoluble in water or ligroine; nearly insoluble in cold ethyl or methyl alcohol, more soluble when hot, but still sparingly; the solubility in glacial acetic acid or acetone is similar, except that it is much more soluble in either of these solvents when hot than it is in alcohol; readily soluble in hot benzol or chloroform; very soluble in ether or carbonic disulphide.

Although pentabromnitrobenzol was the usual impurity, on one occasion a different product was obtained, which consisted of small needles melting, after crystallisation from benzol, at about 312° , essentially insoluble in alcohol or sodic hydrate, and containing no nitrogen. We inferred therefore that this was the hexabrombenzol, which is said to melt above 315° and to be almost insoluble in boiling alcohol, and this inference was proved to be correct by the following analysis:

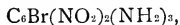
0.1303 gram of the substance gave, by the method of Carius, 0.2666 gram of argentic bromide.

	Calculated for C_6Br_6 .	Found.
Bromine	86.96	87.10

Preliminary Experiments.

After the tetrabromdinitrobenzol had been prepared, the following experiments were tried to determine the ease with which it reacted with various substances.

As has been stated in an earlier paper, alcoholic ammonia has no action on tetrabromdinitrobenzol in the cold, or even if the substances are heated together in open vessels. If, however, the mixture is heated to 100° in a sealed tube for four or more hours, a reaction takes place, giving an orange precipitate and a red alcoholic solution in addition to some unaltered tetrabromdinitrobenzol. The orange insoluble substance was undoubtedly the bromtriamidodinitrobenzol, but, as it was insoluble in all the common solvents, we could only try to purify it by washing, and even after repeated treatment with water, alcohol, chloroform and benzol, were unable to obtain a substance giving constant results on analysis; the bromine varied in different samples from 25.34 to 29.07 per cent., the amount required by the formula,



being 27.39. Although it is probable that further work on this substance would have enabled us to find a method of purifying it, we did not think it worth while to sacrifice the time, as these analyses show that the reaction has run in the same way as that between tribromdinitrobenzol and alcoholic ammonia, and nothing of interest was likely to be found in its investigation. The substance is an orange-yellow powder, insoluble in all the common solvents, and not melting even at 285° . The alcoholic filtrate

contained a yellow substance melting at 185° in the crude state, but we did not obtain enough of it for investigation. With aniline a more favorable result was obtained, which is described fully in the next section of this paper.

When boiled with potassic sulphocyanate in alcoholic solution in a flask with a return condenser, there was very little action, but, if amyl alcohol was substituted for ethyl alcohol, so that the action would take place at a higher temperature, a dark red substance was formed, insoluble in all the common solvents. In this respect the tetrabromdinitrobenzol behaved exactly like the tribromdinitrobenzol, and, as it had been found impossible to purify the corresponding product from the tribrom compound, we did not think it worth while to continue work in this direction.

With sodium malonic ester or sodium acetacetic ester it behaves like the tribromdinitrobenzol. The action with sodium malonic ester is described in detail later in this paper.

In all the derivatives of tetrabromdinitrobenzol which were analysed it was found that only three of the atoms of bromine had been attacked. We had hoped to try some experiments at higher temperatures for the purpose of replacing the fourth atom of bromine, but the work described in this paper has taken so much time that we have been unable to take up this branch of the subject.

Bromdinitrotrianilidobenzol, $C_6Br(NO_2)_2(C_6H_5NH)_3$.

To prepare this substance tetrabromdinitrobenzol was heated with aniline in the proportion of one molecule of the former to a little more than six of the base. Convenient amounts were 7 grams of tetrabromdinitrobenzol to 8.3 grams of aniline. When the mixture was heated on the water-bath the solid dissolved after some time, the solution being accompanied by a change of color from yellow to bright red, and on cooling the whole solidified to a mass of red needles; but in order to get even a tolerable yield of the new substance the heating on the water-bath must be continued for at least four to six hours, and then it is not by any means complete. A higher heat than the water-bath should not be used, as then the mixture shows a tendency to pass into a purplish coloring matter, resembling impure rosaniline in appearance and similar to the substance obtained in the same way from tribromtrinitrobenzol,¹ and like that undoubtedly produced by

¹ This Journal **10**, 291 (1888).

the nitro groups taking part in the reaction. If the reaction had run properly, the product consisted of a viscous or crystalline mass of the color of red lead, from which in the first place the aniline bromide and excess of aniline were removed by washing with water containing a little hydrochloric acid, leaving a brick-red powder. The purification was completed by crystallisation from alcohol, and afterward from a mixture of alcohol and chloroform, until it showed the constant melting point 175° – 176° . If there was difficulty in obtaining crystals of the proper melting point, it was found advisable to warm the substance again with aniline for two or more hours, and then purify again in the manner just described. In addition to unaltered tetrabromdinitrobenzol a small amount of an impurity was found, which melted in the crude state between 120° and 140° , but we did not succeed in isolating a substance fit for analysis from it. The main product, when pure, was dried at 100° , and analysed with the following results:

I. 0.1667 gram of the substance gave 20.4 cc. of nitrogen at a temperature of 25° and a pressure of 768.4 mm.

II. 0.1624 gram of the substance gave, by the method of Ca-rius, 0.0578 gram of argentic bromide.

	Calculated for $C_6Br(NO_2)_2(C_6H_5NH)_3$.	Found.	
		I.	II.
Nitrogen	13.46	13.81	...
Bromine	15.38	...	15.15

Properties.—Bromtrianilidodinitrobenzol forms a brilliant but rather dark red crystalline powder, which, when examined with the microscope, consists of crystals of two forms, rather short prisms terminated by an obtuse angle, and thick groups shaped like an hour-glass and made up of short prisms which seem to have the same terminal angles as those which are not in groups; the groups are rather darker in color than the free prisms, but this is probably due to their being thicker. When crystallised from hot alcohol, instead of the usual mixture of alcohol and chloroform, characteristic forms like sheaves were obtained, also a small quantity of red, nearly square plates. It melts at 175° – 176° ; is essentially insoluble in ligroine, or in water either cold or boiling; very slightly soluble in cold alcohol, more soluble in hot; more soluble in methyl than in ethyl alcohol; slightly soluble in cold ether, freely in hot; moderately soluble in glacial acetic acid;

freely soluble in benzol, chloroform, or carbonic disulphide; very freely in acetone. The best solvent for it is a mixture of alcohol and chloroform, as it tends to separate in a viscous state from the solution in chloroform alone. Strong sulphuric acid dissolves it slightly, forming a pale yellow solution. Strong nitric acid acts in the same way, but less energetically; fuming nitric acid acts upon it violently even in the cold. Hydrochloric acid has no action either hot or cold. The absence of basic properties is accounted for by the presence of the two nitro groups. We tried also the action of sodic hydrate, as certain nitroamido compounds possess weak acid properties,—for instance, the trinitrotoluidine of Nölting and Salis,¹—but found that it produced no effect.

Dibromdinitrophenylmalonic Ester,



This substance was prepared by acting on one molecule of tetrabromdinitrobenzol with about four molecules of sodium malonic ester, as follows: 15 grams of tetrabromdinitrobenzol dissolved in about 20–30 cc. of benzol were mixed with 20 grams of malonic ester previously converted into sodium malonic ester by treatment with the sodic ethylate made from 3 grams of sodium dissolved in 100 to 150 cc. of absolute alcohol. The action began at once, as shown by the appearance of a dark red color and a considerable evolution of heat, so that the flask became too hot to hold in the hand with comfort; in this respect it differed from that with the tribromdinitrobenzol, as, although in that case the red color appeared at once, no perceptible rise of temperature was observed in any part of the reaction. To make certain that the reaction had run as far as possible, the mixture was allowed to stand in the cold for three or four days. At the end of this time the product was diluted with about half a liter of water, and the benzol separated from the red aqueous solution of the salt of the new substance. Upon adding dilute sulphuric acid to this aqueous solution, the new substance was precipitated, and after washing with water was purified by crystallisation from alcohol until it showed the constant melting point 89° , when it was dried *in vacuo* for analysis. The benzol solution, which separated on the addition of water, was evaporated to dryness, and the residue, consisting of the new substance, a little unaltered tetrabromdinitro-

¹ Ber. d. chem. Gesell. 15, 1864.

benzol, and an oil, after being freed from the oil on the pump, was treated with alcohol, in which the tetrabrom compound is essentially insoluble, and the small amount of the new substance thus obtained was added to that from the aqueous solution.

I. 0.2183 gram of the substance gave on combustion 0.2568 gram of carbonic dioxide and 0.0528 gram of water.

II. 0.2144 gram of the substance gave 11.4 cc. of nitrogen at a temperature of 23.1° and a pressure of 763.4 mm.

III. 0.2372 gram of the substance gave, by the method of Carius, 0.1833 gram of argentic bromide.

	Calculated for $C_6HBr_2(NO_2)_2CH(CO_2C_2H_5)_2$.	I.	Found. II.	III.
Carbon	32.23	32.07
Hydrogen	2.48	2.69
Nitrogen	5.78	...	6.02	...
Bromine	33.06	32.91

The yield of dibromdinitrophenylmalonic ester was very satisfactory. On one occasion 5 grams of tetrabromdinitrobenzol gave 4 grams of the dibromdinitrophenylmalonic ester, instead of the 5 grams required by the theory, that is, 80 per cent. of the theoretical yield. This large yield proves conclusively that dibromdinitrophenylmalonic ester is the only aromatic product of the reaction, a point which before this observation seemed somewhat doubtful in the analogous preparations described in other papers from this laboratory, as in them the yield rose but little above 50 per cent. of the theory.

The amount of bromine separated as bromide of sodium in the preparation of the substance was determined in two cases, as follows:

I. 5 grams of tetrabromdinitrobenzol yielded 3.707 grams of argentic bromide, corresponding to 1.578 gram of bromine.

II. 5 grams of tetrabromdinitrobenzol yielded 3.631 grams of argentic bromide, corresponding to 1.545 gram of bromine.

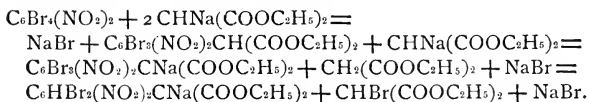
The theoretical yield, if two of the atoms of bromine had been removed, would be 1.653 gram.

Percentage of bromine found as bromide of sodium:

I.	II.
95.43	93.48

From these numbers it appears that essentially all the bromine is removed as sodic bromide.

The oil which formed the secondary product of the reaction was not investigated further, as from the composition of the ester, and the fact that all the bromine appeared as sodic bromide, there could be no question that the nature of this action is the same as that with the tribrom compounds; and in those cases¹ the study of the oils has shown conclusively the mode of formation of the substances. There can be no doubt, therefore, that the reactions which take place in this case should be written as follows:



The brommalonic ester being converted afterward into tartronic or acetylentetracarboxylic ester.

Properties.—The dibromdinitrophenylmalonic ester crystallises from alcohol usually in slightly yellow to colorless needles, which unite into groups like pompons if the solution is dilute; seen under the microscope they consist of rather long rhombic plates with a decidedly acute angle about six times as long as their breadth, or even slenderer, either free or in radiating groups, the crystals branching so as to give the effect of being arranged in curved lines. When less well developed the groups are made up of fine needles very much branched, like certain feathery seaweeds. From the oil which forms the secondary product in its preparation the substance crystallises in flattened prisms, often two centimeters in length, arranged in slightly radiating groups. The melting point is 89°. It is essentially insoluble in water or ligroine, slightly soluble in cold, freely in hot methyl or ethyl alcohol; freely soluble in carbonic disulphide, glacial acetic acid, or acetone; very freely in ether, benzol, or chloroform. Strong sulphuric acid has little, if any, action on it in the cold, but dissolves it slightly without change of color when hot. Strong nitric acid also seems not to act upon it in the cold, but, when warmed with it, turns yellow and imparts a yellow color to the drops of the melted substance which swim on its surface. Hydrochloric acid does not seem to act upon it in open vessels, either cold or warm, although from analogy with the corresponding monobrom compound it is fair to suppose that it would decompose it if the two substances were heated to 150° in a sealed tube.

¹ This Journal **11**, 544 (1889); **12**, 14 (1890).

The dibromdinitrophenylmalonic ester has well marked acid properties, as was to be expected from the fact that one of its atoms of hydrogen is attached to a carbon atom in direct contact with two carboxylester radicals and a dinitrophenyl. An excess of sodic hydrate in aqueous solution has but little action on the solid, turning it pale red; if, however, a drop of alcohol is added it turns a very dark red at once, and the salt begins to dissolve. Potassic carbonate acts in much the same way. Acid sodic carbonate in aqueous solution has no effect, but if alcohol is added there is a slight action, shown by formation of a little of the red salt. Ammonic hydrate in aqueous solution has but little action, but turns red if a little alcohol is added, and upon warming this mixture a deep brownish red solution is obtained, which smells strongly of ammonia, even if an excess of the ester is used in making it. It seems to be decomposed by heating, or by exposure to the air, so that the ammonium salt must be a very unstable substance. The solution of the ammonium salt made with an excess of the ester (but still smelling of ammonia) was treated with various reagents, and gave the following characteristic precipitates:

With a salt of *magnesium, calcium, strontium, or barium*, very heavy pale red flocks.

With a *zinc* salt, pale yellow flocks.

With a salt of *manganese, cobalt, or nickel*, pale red flocks.

With a *ferric* salt, pale brownish purple.

With a *cupric* salt, bright yellow.

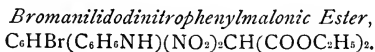
With salts of *mercury*, pale red.

With a *cadmium* salt, reddish yellow.

With a *lead* salt, whitish red.

With a *silver* salt, pale orange.

Strong nitric acid gave with the salts a white precipitate, probably the unaltered ester. In this respect it differs from bromtrinitrophenylmalonic ester.



This substance was made by adding aniline to the dibromdinitrophenylmalonic ester in the proportion of a little more than two molecules of the base to one of the ester. The reaction began in the cold, but was brought to an end by warming the mixture for a short time on the water-bath. The product, after washing with

water, to which a little hydrochloric acid was added to remove aniline bromide and the excess of aniline, was crystallised from hot alcohol until it showed the constant melting point 127° , when it was dried at 100° , and analysed with the following result:

0.2003 gram of the substance gave 14.85 cc. of nitrogen at a temperature of 20.5° and a pressure of 762 mm.

Nitrogen	Calculated for	Found.
	$C_6HBr(C_6H_5NH)(NO_2)_2CH(CO_2C_2H_5)_2$.	
	8.47	8.49

Properties.—The bromanilidodinitrophenylmalonic ester crystallises from alcohol in bright red needles, which under the microscope are seen to be slender prisms terminated usually by two planes, less commonly by one, and seeming to belong to the monoclinic system. The substance melts at 127° , and is essentially insoluble in cold water, very sparingly soluble in boiling water, as shown by the faint yellow color imparted to the liquid; insoluble in ligroine; very slightly soluble in cold ethyl or methyl alcohol, more freely in either of these solvents when hot; slightly soluble in ether; soluble in benzol or glacial acetic acid; freely soluble in chloroform, carbonic disulphide, or acetone. Strong sulphuric acid dissolves it slightly, forming a yellowish solution; the solubility did not seem to be increased by heat. Strong nitric acid dissolved it rather more freely than sulphuric acid, and the solubility was increased by heat. Strong hydrochloric acid had no action upon it, although it is probable that long heating in a sealed tube with this acid would have decomposed it in the way described¹ under the bromdinitrophenylmalonic ester.

The acid properties of this substance have been much weakened by the replacement of bromine by the basic aniline radical C_6H_5NH , but that they still exist is shown by the following observations. Sodic hydrate in aqueous solution has no action on the solid, but on the addition of a little alcohol a dark red solution of the salt is formed; sodic carbonate in aqueous solution produces no effect, but on the addition of alcohol a very slight red coloration appears; acid sodic carbonate produces no effect even in presence of alcohol. Ammonic hydrate in aqueous solution does not dissolve the solid substance, and, even if alcohol is added, the action is very slight; if, however, the mixture of aqueous ammonic hydrate, alcohol, and the solid is warmed on the water-bath, a dark

¹ This Journal **11**, 548 (1889).

red solution is obtained, which smells of ammonia, even if a large excess of the ester is used. The behavior of such a solution with various reagents was studied with the following results:

Salts of *magnesium, calcium, strontium, or barium* gave rusty brown precipitates.

The salts of the heavy metals gave yellow precipitates, except where the color was modified by the excess of ammonia, which could not be removed from the solution of the salt.

Reduction of Dibromdinitrophenylmalonic Ester.

The investigation of this subject interested us especially, because it seemed probable that the diamidophenylmalonic or acetic acid, which would be the first product of the reaction, would lose water and become converted into an amidooxindol, especially since Bischoff¹ obtained from the reduction of his orthonitrobenzoylmalonic ester α - γ -dihydroxychinoline. As with zinc and alcoholic hydrochloric acid, or with zinc dust and acetic acid, he obtained more complex products, some of which it was almost impossible to purify, we decided to try first the action of tin and hydrochloric acid with alcohol upon our dibromdinitrophenylmalonic ester, and for this purpose proceeded as follows: Two grams of the dibromdinitrophenylmalonic ester were mixed with alcohol, strong hydrochloric acid, and tin, a piece of platinum foil being used to accelerate the action, and the mixture was kept upon a steam radiator at a temperature of from 50°–70° until the whole of the malonic compound had disappeared, which usually happened in an hour and a half. The clear solution was poured off from the excess of tin, and, after evaporation to dryness, dissolved again in water, and freed from tin with sulphuretted hydrogen; upon concentrating the filtrate long needles separated, which varied in color from brown to nearly white. By further concentration of the mother-liquors a fresh crop of crystals was obtained, and the precipitate of sulphide of tin must be boiled out several times with water, as the reduction-product is but slightly soluble. As the substance seemed to be decomposed to a certain extent by our attempts to purify it by crystallisation, we analysed some of it without further purification, while other samples were crystallised once more from hot water, allowing the solution to

¹ Ann. Chem. 251, 364.

cool *in vacuo* to avoid oxidation by the air. It was dried *in vacuo*, and analysed with the following results:

I. 0.0977 gram of the substance gave on combustion 0.1224 gram of carbonic dioxide and 0.0434 gram of water.

II. 0.3108 gram gave on combustion 0.3869 gram of carbonic dioxide and 0.1128 gram of water.

III. 0.1113 gram of the substance gave 9.8 cc. of nitrogen at a temperature of 25.5° and a pressure of 763 mm.

IV. 0.1010 gram of the substance treated with argentic nitrate and the precipitate washed with nitric acid and water gave 0.0498 gram of argentic chloride.

V. 0.4762 gram gave 0.2461 gram of argentic chloride.

	I.	II.	Found. III.	IV.	V.
Carbon	34.17	33.93
Hydrogen	4.93	4.03
Nitrogen	9.84
Chlorine	12.19	12.77

The free base corresponding to this chloride was next prepared by adding ammoniac hydrate to a strong solution of it, when a white precipitate swimming in a dark green liquid was obtained. It was purified by washing with cold water, in which it is as good as insoluble, until the wash water gave no test for a chloride, then dried *in vacuo*, and analysed with the following results:

I. 0.1690 gram of the substance gave on combustion 0.2587 gram of carbonic dioxide and 0.0580 gram of water.

II. 0.2021 gram of the substance gave 23.7 cc. of nitrogen at a temperature of 24.5° and a pressure of 768.5 mm.

	I.	Found. II.
Carbon	41.75	...
Hydrogen	3.81	...
Nitrogen	...	13.28

The following comparison shows that the numbers obtained from the analyses of the chloride correspond to those calculated for the formula $C_8H_{11}BrN_2O_2HCl$ (with the exception of the hydrogen,¹ which was undoubtedly brought too high by the passing over of a part of the halogen into the sulphuric acid tube).

¹ The formula $C_8H_{11}BrN_2O_2HCl$ requires 4.23 per cent. of hydrogen, and is therefore distinctly too high for Analysis II, and the analysis of the "chloride of the free base" given later. The small amount of substance used in Analysis I makes the per cent. of hydrogen in it of no value.

	Calculated for $C_8H_5BrN_2O_2HCl$.	Found.	
Carbon	34.12	34.17	33.93
Hydrogen	3.55	4.93	4.03
Nitrogen	9.95	9.84	...
Chlorine	12.61	12.19	12.77

On the other hand, the numbers given by the analyses of the free base indicate a substance containing one molecule less of water.

	Calculated for $C_8H_7BrN_2O$.	Found.	Calculated for $C_8H_9BrN_2O_2$.
Carbon	42.30	41.75	39.17
Hydrogen	3.08	3.81	3.67
Nitrogen	12.34	13.28	11.43

The want of agreement between the percentages of hydrogen¹ is explained in the same way as in the analyses of the chloride. Otherwise the numbers come as near as could be expected, when it is remembered that the free base was so unstable that we did not dare to purify it except by washing, and that it gradually turned brown even when dry.

In order to harmonise these results and determine the nature of the substances we have found only three hypotheses.

First, and most obvious. The two substances belong to different classes, *i. e.* one is the chloride of the bromdiamidophenylacetic acid, $C_6H_2BrNH_2ClNH_2CH_2COOH$; the other is free bromamidooxindol, $C_6H_2BrNH_2(CH_2CONH)$.

If, on the other hand, the substances belong to the same class,—

Second. They are the bromamidooxindol and its chloride. In this case the chloride must contain one molecule of water of crystallisation.

Third. They are bromdiamidophenylacetic acid and its chloride. In this case our analyses of the free base are incorrect.

If the first of these explanations is the true one, the chloride made by adding hydrochloric acid to the free base would be the chloride of the bromamidooxindol, and therefore different from the original chloride of the bromdiamidophenylacetic acid. To settle this point, we set free the base with ammonic hydrate from a quantity of the original chloride, and, after washing until free from ammonic chloride, dissolved it in dilute hydrochloric acid and crystallised it from the slightly acid solution. The general habit of the crystals of the two chlorides (the original one and that

¹ The formula $C_8H_9BrN_2O$ requires 3.93 per cent. of hydrogen.

made from the free base) was the same, but there were differences in the modifications on the ends of the prisms which made the identity of the two somewhat doubtful; we accordingly analysed the chloride made from the free base, with the following results:

0.1853 gram of the substance gave on combustion 0.2328 gram of carbonic dioxide and 0.0678 gram of water.

	Calculated for $C_8H_7BrN_2OHCl$.	Calculated for $C_8H_9BrN_2O_2HCl$.	Found.	Analyses of Original Chloride.	
Carbon	36.43	34.12	34.26	34.17	33.93
Hydrogen	3.04	3.55	4.06	4.93	4.03

There can be no doubt, therefore, of the identity of the two chlorides, and the first explanation must be abandoned.

The second explanation requires that the chloride should contain one molecule of water of crystallisation. This point was tested by heating the chloride with the following result:

0.2517 gram of the chloride heated for 6 hours at first at 110° , later to 135° , lost 0.0024 gram.

	Calculated for $C_8H_7BrN_2OHClH_2O$.	Found.
Water	6.42	0.95

From this it appears that, if the chloride contains water of crystallisation, it does not lose it at 135° . The slight loss of only 2.4 mgrs. could be sufficiently accounted for by the decomposition of the salt which had turned dark gray on the surface, and for this reason too the heating could not be repeated at a higher temperature.

This result, unfavorable to the second explanation, necessitates the discussion of the third—that the free base is bromdiamidophenylacetic acid—which otherwise we should not have thought worthy of consideration. As has been already stated, the analyses of the free base do not agree with this explanation, and in order to adopt it we must assume that the substance had undergone a decomposition sufficient to raise the carbon 2.58 per cent., an assumption improbable in itself and not supported by the appearance of the preparation, which had only a slight dirty pink color. This we think is enough to condemn this third explanation, but we add the following considerations, all of which tell strongly in favor of the second and against the third explanation. (1) Gabriel and R. Meyer¹ by the reduction of dinitrophenylacetic acid with

¹ Ber. d. chem. Gesell. 14, 832.

tin and hydrochloric acid obtained the paramidooxindol direct, and it does not seem possible that our bromdiamidophenylacetic acid, which differs from theirs only in containing an atom of bromine, should be so much more stable. (2) Our free base agrees fairly well in properties with the paramidooxindol of Gabriel and R. Meyer. Both are easily oxidised, soluble in hot water or in alcohol, slightly soluble in benzol or carbonic disulphide, the only difference being that our base is nearly insoluble in ether, whereas theirs is soluble in it. The melting points also stand about where we should expect, amidooxindol about 200° , our bromamidooxindol about 212° ; in both cases there was so much blackening that the melting point could not be accurately determined. (3) Our base (or its chloride) gives the indol reaction, turning a piece of pine wood red if boiled with it and dilute sulphuric acid, or if the wood, after being saturated with a solution of the base, is soaked in strong hydrochloric acid. This seems to us conclusive. The color is rather dull, and appears only after some time; but the objection which might be urged against this argument on this account, that the bromdiamidophenylacetic acid was converted into the bromamidooxindol by treatment with the acids, has no weight, as in the preparation of the original chloride it was most thoroughly exposed to the action of strong hydrochloric acid, both hot and cold; and yet this chloride, as we have shown by the analyses, contained two atoms of hydrogen and one of oxygen more than is required by the chloride of the bromamidooxindol.

These arguments seem to us to prove conclusively that the two substances are bromamidooxindol $C_6H_2BrNH_2(CH_2CONH)$, and its chloride $C_6H_2BrNH_2(CH_2CONH)HCl.H_2O$, in spite of the fact that we could not drive off the water of crystallisation from the chloride even at 135° .

Properties of Bromamidooxindol, $C_6H_2BrNH_2(CH_2CONH)$.

As precipitated from its chloride it forms a heavy flocculent white precipitate, which, when examined with the microscope, is seen to be a felt of small white needles, often arranged in fagots or groups like an hour-glass; it is not very stable, changing to a dirty pink on exposure to the air, even when dry. The substance analysed melted at 212° with a good deal of blackening, but we do not place much reliance on this melting point, as the sample used was a good deal colored. It is almost insoluble in cold, soluble

in hot water ; soluble in hot alcohol ; insoluble, or nearly so, in ether or chloroform ; not freely soluble in benzol or carbonic disulphide, even when hot ; freely soluble in hot glacial acetic acid. Sodid hydrate dissolves it, giving a pinkish or pale magenta solution ; ammoniac hydrate at first seems to have no action, but on standing the liquid and solid turn dark bluish green ; potassic carbonate in aqueous solution does not dissolve it. It seems therefore to have the properties of a phenol. Neither picric acid in benzol solution, nor ferric chloride with an alcoholic solution of the base, produced any change of color. If some of the free base was boiled with dilute sulphuric acid and a piece of pine, the wood was turned a dull orange-red.

As to the constitution of this base it has been determined by work¹ done in this laboratory on the bromdinitrophenylmalonic ester that the nitro group, from which the amido group is formed, is in the para position to the carbon side-chain. The bromine is probably in the ortho position, since all our work with the tetrabromdinitrobenzol has shown that only three of its atoms of bromine can be replaced easily ; and, as the compounds made from this substance are so closely analogous to those prepared from the tribromdinitrobenzol, it is fair to infer that the three symmetrical (meta) atoms of bromine are those which can be removed, and that the fourth more stable atom of bromine is the one in the unsymmetrical (ortho) position ; the atom of bromine, therefore, which reduction takes away from the dibromdinitrophenylmalonic ester, would be that in the meta position, and the base would be accordingly *orthobromparamidooxindol*.

Properties of the Chloride of Bromamidooxindol,



When crystallised from water the substance forms needles, or prisms, sometimes as much as a centimeter long and a millimeter thick, which seem to belong to the monoclinic system, and usually have a yellowish color ; we think, however, that this color is due to partial oxidation, and that the substance is white when pure. When examined with the microscope the prisms are found to be arranged in globular radiating groups, and are terminated usually by a single rhombic plane at a not very oblique angle to the long sides of the prism ; sometimes a number of other modify-

¹ This Journal **11**, 556 (1889).

ing planes are observed, giving a sharp end to the prism. From alcohol it crystallises in branching needles set at a very acute angle to each other. It melts only at a very high temperature, probably above the range of the mercury thermometer. It is slightly soluble in cold water, freely in hot; soluble in alcohol; slightly soluble in cold benzol, chloroform, or glacial acetic acid, freely soluble in these solvents, when hot; almost insoluble in ether; very soluble in carbonic disulphide. The best solvent for the substance is boiling water. An excess of ammoniac hydrate throws down from a concentrated solution a heavy precipitate of the free base, which is white, but the liquid turns dark green; potassic carbonate gives a similar precipitate, not soluble in an excess; sodic hydrate in small quantity gives a similar precipitate, but dissolves it when added in larger quantity, giving a reddish solution. It gives a dull orange-red indol reaction with pine wood.

LXIX. — GENERAL CONSIDERATIONS IN REGARD
TO CERTAIN COMPOUNDS PREPARED
FROM BROMNITROBENZOLS.¹

BY C. LORING JACKSON.

Several compounds derived from various bromnitrobenzols have been described recently by me in conjunction with other chemists in a number of papers² from this laboratory, but in the course of the work certain general observations were made in regard to them which could not conveniently be introduced in the separate papers, and are therefore collected here.

The Action of Sodium Malonic (or Acetacetic) Ester on Certain Bromnitrobenzols.

The actions studied were the following :

Sodium Malonic Ester on

Tribromtrinitrobenzol, $C_6Br_3(NO_2)_3$, melting point 285° .

Tribromdinitrobenzol, $C_6HBr_3(NO_2)_2$, melting point 192° .

Tetrabromdinitrobenzol, $C_6Br_4(NO_2)_2$, melting point 228° .

Sodium Acetacetic Ester on

Tribromdinitrobenzol, $C_6HBr_3(NO_2)_2$, melting point 192° .

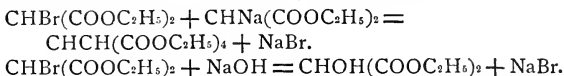
¹ Communicated by the author, from the Proceedings of the American Academy of Arts and Sciences.

² This Journal **10**, 283; **11**, 93, 448, 541; **12**, 7, 164, 289.

In all these cases the action was essentially the same, and may be represented by the following reactions for tribromtrinitrobenzol:

- I. $\text{C}_6\text{Br}_3(\text{NO}_2)_3 + \text{CHNa}(\text{COOC}_2\text{H}_5)_2 =$
 $\text{NaBr} + \text{C}_6\text{Br}_2(\text{NO}_2)_3\text{CH}(\text{COOC}_2\text{H}_5)_2.$
- II. $\text{C}_6\text{Br}_2(\text{NO}_2)_3\text{CH}(\text{COOC}_2\text{H}_5)_2 + \text{CHNa}(\text{COOC}_2\text{H}_5)_2 =$
 $\text{C}_6\text{Br}_2(\text{NO}_2)_2\text{CNa}(\text{COOC}_2\text{H}_5)_2 + \text{CH}_2(\text{COOC}_2\text{H}_5)_2.$
- III. $\text{C}_6\text{Br}_2(\text{NO}_2)_2\text{CNa}(\text{COOC}_2\text{H}_5)_2 + \text{CH}_2(\text{COOC}_2\text{H}_5)_2 =$
 $\text{C}_6\text{HBr}(\text{NO}_2)_2\text{CNa}(\text{COOC}_2\text{H}_5)_2 + \text{CHBr}(\text{COOC}_2\text{H}_5)_2.$

The formation of brommalonic ester in III, the only point in these reactions about which there was any doubt, was proved by the isolation of acetylentetracarboxylic ester¹ or of tartaric acid² from the oily secondary product, as these substances could hardly have been formed otherwise than by the following reactions:



Reactions I-III are given because they show more clearly what has taken place, but the discussion which follows does not depend on them alone, since the analyses of the products are sufficient to prove that in all the cases studied the action has consisted in the replacement of one atom of bromine by the malonic ester radical, and of the second by hydrogen, while the third (and fourth) has remained unaltered.³ This difference in the behavior of the three atoms of bromine is certainly very curious, and, so far as I can find, no case analogous to it has been described as yet. The strangeness of the replacement of bromine by hydrogen becomes especially evident when it is remembered that in every case there was a large excess of sodium malonic ester present, and that this second atom of bromine has therefore combined with the carbon of malonic ester (see Reaction III) in preference to the sodium of sodium malonic ester, so that the tendency to introduce hydrogen rather than the malonic ester radical has been strong enough in this case to overcome the attraction of the bromine for the sodium, and to cause it to combine with carbon instead.

I have not succeeded in finding any explanation of these curious observations which satisfies me, but hope to be led to one by further experiment. It can be stated at present, however, that the difference

¹ This Journal **12**, 16 (1890).

² Ibid. **11**, 546 (1889).

³ In the trinitro compound the third atom of bromine is replaced by the malonic ester radical to a limited extent even in the cold, but it is acted on much less easily than the first.

of behavior in the three bromine atoms is not due to differences in their position on the benzol ring. This is shown easily in the case of the tribromtrinitrobenzol, as here the three atoms of bromine occupy exactly similar positions, each being ortho to two nitro groups and para to the third. In the tribromdinitrobenzol,¹ also, the first and third atoms of bromine are similarly placed (ortho to one, para to the other nitro group), but the second (that replaced by hydrogen) is peculiar in being ortho to both nitro groups. It is evident, then, that in these reactions both similarly placed bromine atoms are not replaced by the malonic ester radical; but it is also to be observed that the bromine which is replaced by hydrogen has in every case stood in the ortho position to two nitro groups, and this suggested to me that perhaps an atom of bromine in this position might be especially susceptible to the action of free malonic ester. To test this hypothesis I mixed some tribromdinitrobenzol dissolved in benzol with malonic ester, and, after the mixture had stood for some time in the cold, warmed it for about an hour on the water-bath, but even after this treatment no action² had taken place, as the tribromdinitrobenzol melted unaltered at 192°. This result was confirmed by a similar experiment with acetacetic ester, which stood with tribromdinitrobenzol for six months without any action. It is evident, therefore, that this atom of bromine is not attached in an especially loose way to the molecule, and that its replacement by hydrogen does not depend only on its position with reference to the nitro groups, but is due also to the presence of the malonic ester radical.

On the Relative Ease with which the Reactions take Place.

This subject will, I hope, prove susceptible of quantitative treatment, and I propose next year to try some experiments of this sort; I shall, therefore, at present confine myself to two qualitative observations, which were so marked that a quantitative confirmation of them seems unnecessary.

The tribromtrinitrobenzol is distinctly more reactive than the tribromdinitro- or tetrabromdinitrobenzol, as it acts on alcoholic ammonia in the cold, whereas the other two must be heated to 100° in sealed vessels to bring about this reaction.

¹ In the tetrabromdinitrobenzol the fourth atom of bromine seems to have no influence on the reaction, and therefore all I say about the tribromdinitrobenzol also applies to this substance.

² The addition of a little aqueous sodic hydrate was enough to cause action at once, as shown by the appearance of the red color of the sodium salt.

The sodium acetacetic ester acts much less energetically than sodium malonic ester upon tribromdinitrobenzol, since the red color of the product appears instantaneously with the malonic ester, but only after some time with acetacetic ester, and the yield of the acetacetic compound is much smaller than that of the malonic derivative, if the reactions are carried on under the same conditions.

On the Acidity of the substituted Malonic Esters, Acetacetic Ester, and Ketones described in the preceding Papers.

In order to determine the relative acidity of these substances, their action with the following reagents was studied: acid sodic carbonate, sodic carbonate, ammoniac hydrate, sodic hydrate. Each reagent was added in aqueous solution to the solid organic substance, and, after observing what took place, alcohol was added, and any change in the behavior of the substance noted. All these experiments were tried at the same time, great care being used to make the conditions as nearly the same as possible. The results can be divided into those which were perfectly definite, that is, where the differences consisted in the fact that one compound formed a salt with the reagent, and another did not; and those depending to a certain extent upon my judgment, in which the differences were only in the amount of salt formed, as shown by the depth of color, or in the quantity of alcohol necessary to produce the salt. The differences of the first class can be described most clearly and succinctly by the following table, in which the substances are arranged in the order of their acidity, beginning with the most acid. The columns correspond to the reagents, and the word "Salt" indicates that a salt was formed, as shown by the color imparted to the solution, or solid.

The observations recorded in this table divide these substances into the following groups (indicated by the lines):—I and II, most acid; III, IV and V, less acid; VI, less acid; VII, less acid; VIII, least acid. The relative acidity of I and II was determined by data of the second sort mentioned above, since I gave a much stronger coloration than II with aqueous sodic carbonate, ammoniac hydrate, or sodic hydrate. The order of III, IV and V was determined by the following observations: With acid sodic carbonate and dilute alcohol, III and IV gave a stronger red color than V. With aqueous sodic carbonate, III

	NaHCO ₃		Na ₂ CO ₃		NH ₄ OH		NaOH	
	Aqueous.	With Alcohol.	Aqueous.	With Alcohol.	Aqueous.	With Alcohol.	Aqueous.	With Alcohol.
I. $C_6H_2Br(NO_2)_2C_2H_5OCHCO_2C_2H_5$	Salt	Salt	Salt	Salt	Salt	Salt	Salt	Salt
II. $C_6HBr(NO_2)_2CH(CO_2C_2H_5)_2$	Salt	Salt	Salt	Salt	Salt	Salt	Salt	Salt
III. $C_6H_2Br(NO_2)_2CH(CO_2C_2H_5)_2$..	Salt	Salt	Salt	Salt	Salt	Salt	Salt
IV. $C_6H_2Br(NO_2)_2CH_2COCH_3$..	Salt	¹ Salt	Salt	Salt	Salt	Salt	Salt
V. $C_6HBr_2(NO_2)_2CH(CO_2C_2H_5)_2$..	Salt	Salt	Salt	Salt	Salt	Salt	Salt
VI. $C_6H_2C_6H_5NH(NO_2)_2CH(CO_2C_2H_5)_2$..	Salt	..	Salt	..	Salt	..	Salt
VII. $C_6HBrC_6H_5NH(NO_2)_2CH(CO_2C_2H_5)_2$	Salt	..	Salt	..	Salt
VIII. $C_6H_2C_6H_5NH(NO_2)_2CH_2COCH_3$	Salt	Salt

¹ No salt was obtained from IV with aqueous sodic carbonate, but I ascribe this to a mistaken observation, probably due to the difficulty in moistening the ketone with the aqueous solution.

gave a pale red, V a much paler, in fact barely perceptible color. With aqueous ammoniac hydrate, III gave a pale red, V a very pale, barely perceptible red, and IV stood between III and V in color. With aqueous sodic hydrate, the color was confined to the crystals of the organic substance, owing to the slight solubility of the salt in a solution of sodic hydrate, and III turned dark red, IV pale red, while V showed a mixture of pale red particles of the salt and white ones of the ester. Upon adding alcohol to the mixture of the substance and either aqueous sodic carbonate or ammoniac hydrate, a dark red color was obtained from all three, but much more alcohol was necessary to produce this color with V than with III or IV. My observations on the intensity of the color with different reagents confirm the order of compounds VI, VII and VIII, but I do not think it worth while to give the details. I should add, also, to show that the personal equation did not enter to any great extent into these observations, that the substances during the experiments were arranged in an order different from that of their acidity, and that the order of acidity given above derived from these experiments was a surprise to me in many particulars.

These experimental results justify the following inferences in regard to the effect of differences in composition upon the acidity of these substances :

(a). The introduction of an additional nitro group (in the ortho position) increases the acidity, since II is more acid than III.

(*b*). The replacement of hydrogen (in the ortho position) by bromine diminishes the acidity, since V is less acid than III.

(*c*). The replacement of bromine (in the meta position) by the aniline radical C_6H_5NH reduces the acidity very considerably, since III, IV and V are much more acid than VI, VIII and VII respectively.

In all these cases the differences occur in the benzol ring, and the effects are very marked (especially in *c*) when it is considered that the hydrogen affected is attached to the side-chain, and therefore more removed from the influence of the acid radicals than in most of the similar cases previously described, in which the element influenced was attached to the benzol ring. These observations recall some made by me several years ago, when I showed¹ that the ring bromine in the three brombenzylbromides had a marked influence in diminishing the ease with which the side-chain bromine was removed, varying with its position on the benzol ring, the para bromine having less influence than the meta, the meta than the ortho.

(*d*). The nature of the side-chain also has a marked influence on the acidity; thus the substituted acetacetic ester I is much more acid than the corresponding malonic ester III, a result in harmony with Claisen and Ehrhardt's² classification of the radicals according to their acid-producing power, since they give the following list, beginning with that which has the least influence, "phenyl, carboxyl, benzoyl, acetyl, formyl."

An approximate measure of the relative acid-producing power of carboxyl and acetyl is given by the comparison of III and IV, which possess nearly the same degree of acidity, and therefore it follows that one acetyl has nearly, although not quite, the same effect as two carboxyls.

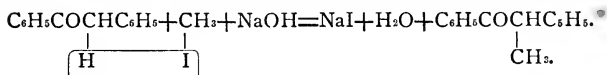
(*e*). The comparison of a dimalonic with the corresponding monomalonic compound in this respect is of interest. Unfortunately I had none of the trinitrophenylendimalonic ester when the comparison described above was made, so that this substance does not appear in the table; but by comparing the observations made on it when its properties were studied with those on the bromtrinitrophenylmalonic ester, I found that the dimalonic compound is much less acid than the brommonomalonic ester, since acid sodic carbonate in aqueous solution has no action upon it,

¹ This Journal 3, 252 (1881).

² Ber. d. chem. Gesell. 1889, p. 1019.

and even aqueous sodic carbonate gives only a very faint red color.¹ This weaker acidity can be accounted for by the hypothesis that the influence of the three nitro groups being divided between two malonic ester radicals, each will have the acidifying influence of only one and a half nitro groups, instead of the three, which act on the acid hydrogen in the monomalonic compound.

The stability of the salts of all these compounds is remarkable, the sodium salt even of the anilidodinitrobenzylmethylketone (the least acid of all these substances) having been prepared and analysed with no especial difficulty; it shows, therefore, a marked difference in this respect from desoxybenzoine ($C_6H_5COCH_2C_6H_5$), the sodium compound of which, according to Victor Meyer,² has not been isolated. In fact, he thinks it probable that it may not exist in the free state, and leaves it doubtful whether the syntheses of homologues of desoxybenzoine are preceded by the formation of a sodium compound, as with malonic or acetacetic ester, or whether the homologue is formed direct by the removal of hydrogen and the halogen by sodic hydrate, according to this reaction:



The reason for this striking difference in acidity between the substituted benzylmethylketones and desoxybenzoine can hardly be due to the fact that the former contain the more active acetyl instead of the benzoyl contained in the latter, although this may have some influence, but in my opinion is rather to be ascribed to the heightening of the acid-producing power of the phenyl by the nitro groups which it contains. The salts of the acetacetic or malonic esters are much more stable than those of the ketones, as was to be expected, since in these cases the hydrogen is exposed to the acidifying power of three radicals (nitrophenyl and two carboxyls, or one carboxyl and an acetyl), and their stability almost equals that of the salts of Bischoff's³ orthonitrobenzoyl-malonic ester, in which the nitrophenyl of my compounds is replaced by the even more acid nitrobenzoyl.

¹ I should be inclined to place the trinitrophenylendimalonic ester between III and V, although from the absence of comparative work its exact place cannot be determined with certainty; this, however, is of little importance, as the comparison of it with II is the only one of especial interest.

² *Ber. d. chem. Gesell.* 1888, p. 1291.

³ *Ann. Chem.* 251, 364.

LXX.—ON CERTAIN DERIVATIVES OF FURFUR-ACRYLIC ACID.

BY H. B. GIBSON AND C. F. KAHNWEILER.,

The preparation of furfuracrylic acid was described by v. Baeyer¹ 1877. At that time, however, the investigation of the acid was pushed in but one direction, and the successive steps by which it could be converted into *α*-pimelic acid were alone described in detail. It seemed that a further study of the acid in other directions also could hardly fail to yield interesting results.

The ready decomposition of furfuracrylic acid by mineral acids compelled us to relinquish the line of work we originally had proposed to follow, and we consequently began an investigation into the nature of this decomposition. The study of the action of hydrochloric acid upon an alcoholic solution of furfuracrylic acid was just beginning to yield us results when the paper of Markwald² upon the same subject reached us, and we were therefore obliged to abandon our work in this direction, and turned our attention to the products formed by the action of bromine, which promised to repay investigation. We felt ourselves quite at liberty to continue our study of furfuracrylic acid in this direction, since Markwald had declared himself unable to obtain well defined crystalline products in this way.

FURFURACRYLIC ACID.

In the preparation of furfuracrylic acid we have found it advantageous to modify slightly the proportions given by v. Baeyer, and in this respect our experience agrees more closely with that of Markwald. We have heated 2 parts of furfural with 3 parts of fused sodic acetate and 3 parts of acetic anhydride with reverse cooler at 160°–170° for about ten hours, extracted the acid with a dilute solution of sodic carbonate, precipitated with hydrochloric acid, and recrystallised the product thus obtained from boiling water. Although the yield varied somewhat in successive preparations, we frequently obtained an amount equal to the weight of furfural employed. The melting point of the pure acid we found to be 140°, in agreement with the observations of Jaffe and Cohn,³ instead of 136° as given by v. Baeyer. From the acid we made the methyl ether and the amide, which we may describe a

¹ Ber. d. chem. Ges. 10, 355.² Ibid. 20, 2811.³ Ibid. 20, 2315.

little more in detail, since no description of them has yet been published.

Methyl Furfuracrylate, $C_7H_5O_3 \cdot CH_3$.—By precipitating with argentic nitrate a solution of ammoniac furfuracrylate, the silver salt was obtained as a heavy curdy precipitate. This was carefully dried and treated with an excess of methyl iodide. When the decomposition was complete the product of the reaction was extracted with ether, and purified by distillation under diminished pressure. Under a pressure of 15 mm. the methyl furfuracrylate distills unchanged at 112° , and the distillate solidifies in beautiful rhombic crystals which melt at 27° . Under a pressure of 774 mm. we found that the ether distilled without apparent decomposition at 227° – 228° . It possessed an agreeable characteristic odor, and dissolved readily in alcohol, ether, ligroin, or benzol. An analysis give the following results:

0.224 gram substance gave 0.5157 gram CO_2 and 0.1084 gram H_2O .

	Calculated for $C_8H_8O_3$.	Found.
C	63.17	63.23
H	5.26	5.42

Furfuracrylamide, $C_7H_5O_2 \cdot NH_2$.—Concentrated aqueous ammoniac hydrate acted but slowly upon methyl furfuracrylate in the cold, but at 100° in sealed tube the decomposition was readily effected. The amide was sparingly soluble in cold water, more readily in hot water, and crystallised in pearly scales which melted at 168° – 169° .

I. 0.4076 gram substance gave 35.5 cc. moist nitrogen at 21.4° and under a pressure of 766 mm.

II. 0.4590 gram substance gave 41.9 cc. moist nitrogen at 21.7° and under a pressure of 767 mm.

	Calculated for $C_7H_7NO_2$.	I. Found.	II.
N	10.22	9.98	10.45

Action of Bromine.

It had already been observed by v. Baeyer that furfuracrylic acid was readily attacked by aqueous bromine, but he had made no careful study of the products formed. Since the product formed in this way was uninviting, and the reaction undoubtedly complicated, it seemed advisable to study instead the action of dry bro-

mine, which might yield well characterised addition products. We soon found, however, that with dry bromine even in the cold substitution was readily effected, so that the simplest well defined product contained three atoms of bromine. Subsequent study showed that this product was a saturated compound in which one atom of bromine had taken its place in the furfuran ring.

Bromfurfurdibrompropionic Acid, $C_7H_5Br_3O_3$.—If furfuracrylic acid is suspended in ten times its weight of carbonic disulphide and two molecules of dry bromine added, a clear deep red solution is at once obtained, from which hydrobromic acid is soon evolved in quantity. Although the reaction progresses steadily at ordinary temperatures, it may be greatly hastened by heat, and we usually have heated the mixture upon the water-bath soon after the addition of the bromine. When the evolution of the hydrobromic acid slackens, and a crystalline substance has separated in quantity, the solution is well cooled, filtered, and the crystalline solid well washed with cold carbonic disulphide. The substance then gives on analysis percentages which closely agree with those required by the formula $C_7H_5Br_3O_3$; but it may still further be recrystallised from hot benzol or carbonic disulphide.

I. 0.2080 gram substance gave 0.3117 gram AgBr.

II. 0.3798 gram of substance recrystallised from carbonic disulphide gave 0.3099 gram CO_2 and 0.0502 gram H_2O .

III. 0.2005 gram substance recrystallised from benzol gave 0.2998 gram AgBr.

IV. 0.2003 gram substance recrystallised from benzol gave 0.2993 gram AgBr.

	Calculated for $C_7H_5Br_3O_3$.	I.	II.	Found. III.	IV.
C	22.28	...	22.26
H	1.33	...	1.47
Br	63.66	63.78	...	63.65	63.60

Bromfurfurdibrompropionic acid crystallises in small flat oblique prisms, which are sparingly soluble in cold benzol or carbonic disulphide, more readily in hot. It is readily soluble in alcohol or ether, insoluble in water, although slowly decomposed by it. On heating, the acid is gradually decomposed, with the evolution of hydrobromic acid and slight carbonisation. As might be expected, we found it impossible to prepare salts, or even ethers, of the acid.

The action of cold water upon the acid was so well marked that

we proceeded to determine the products formed. When bromfurfurdibrompropionic acid is suspended in water, carbonic dioxide soon begins to escape, and after long standing the crystalline solid is completely converted into a colorless oil. The aqueous solution then contains hydrobromic acid in abundance. As the decomposition was greatly facilitated by gentle heat, we usually have allowed the reaction to proceed at about 40°. When the decomposition was complete, we distilled with steam, and dried the heavy colorless oil thus obtained with calcic chloride. On distillation under diminished pressure, we found that this oil began to boil at 108° under a pressure of 14 mm., and that the thermometer gradually rose to 112°, the pressure remaining constant. The distillate was at first nearly colorless, and of high refractive power, but on standing it quite rapidly became dark-colored. Analyses of the freshly distilled substance showed it to be a bromfurfurbromethylen.

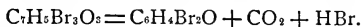
I. 0.3173 gram substance gave 0.3350 gram CO₂ and 0.0476 gram H₂O.

II. 0.1928 gram substance gave 0.2883 gram AgBr.

III. 0.2045 gram substance gave 0.3056 gram AgBr.

	Calculated for C ₆ H ₄ Br ₂ O ₂ .	I.	Found. II.	III.
C	28.57	28.79
H	1.59	1.67
Br	63.49	...	63.65	63.60

The reaction is then strictly analogous to what by which β-bromstyrol may be made from phenyldibrompropionic acid :



The aqueous solution left in the retort after distillation with steam deposited on long standing a small quantity of a crystalline acid. The quantity of this acid was so insignificant that we were able to identify it only after uniting the products obtained in many successive preparations. Two determinations of the percentage of bromine showed the acid to be the bromfurfuracrylic acid subsequently described. Lack of material made it impossible to prove with precision the identity of the two acids, and we can therefore only assert their close resemblance.

I. 0.1262 gram substance gave 0.1091 gram AgBr.

II. 0.1956 gram substance gave 0.1700 gram AgBr.

Br	Calculated for $C_7H_5BrO_2$.	Found.	
		I.	II.
	36.86	36.79	36.99

We have hitherto been unable to find other definite products of the reaction.

By the action of bromine upon bromfurfurbromethylen we could obtain no products which invited further study. On the other hand, alcoholic potassic hydrate gave us the corresponding acetylen derivative, although we have not yet isolated it in a pure condition. The oil obtained as the direct product of the reaction contained much too large a percentage of bromine, and prolonged action at a higher temperature gave no more satisfactory results. That the oil contained the acetylen derivative was readily shown by its behavior with an ammoniacal solution of silver or copper. The silver compound was white, the copper compound a greenish yellow. The latter was made in larger quantity, carefully washed by decantation, and dried over sulphuric acid. It then exploded violently by heat or on contact with fuming nitric acid, and contained the required percentage of copper.

I. 0.6479 gram substance gave by electrolysis 0.1748 gram Cu.

II. 0.6178 gram substance gave 0.1681 gram Cu.

Cu	Calculated for $(C_6H_2BrO)_2Cu_2$.	Found.	
		I.	II.
	27.16	26.98	27.20

From the copper compound we attempted to prepare the bromfurfuracetylen in a pure condition. By decomposing with acid, extracting with ether, and distilling the well dried extract under diminished pressure, we obtained a colorless oil which boiled at 65° – 68° under a pressure of 19 mm. This oil contained a percentage of bromine, which left no doubt as to its identity, but showed at the same time that it was still impure. We have as yet made no further attempt at its complete purification.

It seemed to us of interest to prepare by oxidation the diacetylene derivative also, analogous to the diacetylenylphenyl of Glaser,¹ which was afterward more fully studied by v. Baeyer and Landsberg.² In its preparation we followed closely the method of v. Baeyer. To the copper compound was added one molecule of potassic ferricyanide in aqueous solution. When the oxidation was complete, the precipitate formed was collected on a filter, dried, and extracted with hot alcohol. On cooling the alcohol deposited

¹Ann. Chem. (Liebig) **154**, 159.

²Ber. d. chem. Ges. **15**, 57.

the new compound in small iridescent plates which melted at 126°. It was readily soluble in hot alcohol, sparingly in cold alcohol, and dissolved freely in ether, chloroform, benzol, or ligroin. Analysis showed the substance to be dibromdifurfurdiacetylene (diacetylene-bromfurfuryl):



I. 0.2476 gram substance gave 0.3888 gram CO_2 and 0.0383 gram H_2O .

II. 0.1538 gram substance gave 0.1696 gram AgBr.

III. 0.1548 gram substance gave 0.1702 gram AgBr.

	Calculated for $\text{C}_{12}\text{H}_4\text{Br}_2\text{O}_2$.	I.	Found II.	III.
C	42.36	42.82
H	1.18	1.72
Br	47.06	...	46.93	46.79

BROMFURFURACRYLIC ACID.

The behavior of the acid containing three atoms of bromine which was obtained by the direct action of bromine upon furfuracrylic acid left little doubt that it was a bromfurfurdibrompropionic acid. If this view were correct, it seemed not improbable that the bromine attached to the side-chain might be removed without disturbing the bromine in the furfuran ring, and that a bromfurfuracrylic acid would thus be formed. After a few preliminary experiments it was found that zinc dust added to an alcoholic solution of the bromfurfurdibrompropionic acid brought about the desired result. The reaction is vigorous, and the boiling point of the alcohol soon reached. When the reaction is over, water is added to the filtered solution, and the acid which is thus precipitated is purified by conversion into its sodium salt, reprecipitation with hydrochloric acid, and recrystallisation from dilute alcohol or boiling water. The yield of the new acid thus obtained was between 80 and 90 per cent. of the theoretical amount, and analysis showed that it had the desired composition.

I. 0.2645 gram substance gave 0.3768 gram CO_2 and 0.0566 gram H_2O .

II. 0.2511 gram substance gave 0.2161 gram AgBr.

III. 0.2223 gram substance gave 0.1920 gram AgBr.

IV. 0.1490 gram substance gave 0.1288 gram AgBr.

	Calculated for $C_7H_5BrO_3$.	I.	II.	Found. III.	IV.
C	38.71	38.86
H	2.30	2.38
Br	36.86	...	36.63	36.76	36.80

Bromfurfuracrylic acid crystallises in long slender prisms, which are sparingly soluble in cold water, more readily in hot water. The acid dissolves readily in alcohol, ether, hot benzol, or hot chloroform, in cold benzol or cold chloroform it is but sparingly soluble, and it is nearly insoluble in ligroin. It melts sharply at 176° – 177° , but since it is somewhat decomposed and blackened by long continued heating above 150° , the bath must first be heated to within a few degrees of the melting point. Small quantities of the acid may readily be sublimed between watch-glasses. The sublimed product also melts at 176° – 177° , and darkens upon long heating. With bromine the acid unites readily, and forms the original substituted propionic acid. We have made many attempts to convert the acid into the corresponding substituted pyromucic acid, or to obtain from it by oxidation a product which should enable us to fix the position of the bromine atom, but hitherto without success. We can, therefore, at present only conjecture that the bromine in this case, as with the pyromucic acid, enters first the δ position. For the further characterisation of the acid we have prepared a few of its salts.

Baric Bromfurfuracrylate, $Ba(C_7H_4BrO_3)_2 \cdot H_2O$.—The barium salt is sparingly soluble in cold water, somewhat more readily in hot water, and crystallises in clustered needles. When air-dried it loses nothing over sulphuric acid, gives up one molecule of water slowly at 100° , and is decomposed at a somewhat higher temperature.

I. 1.1830 gram of the air-dried salt lost at 100° 0.0380 gram H_2O .

II. 0.7064 gram of the air-dried salt lost at 100° 0.0227 gram H_2O .

III. 0.4898 gram of the air-dried salt gave 0.1951 gram $BaSO_4$.

	Calculated for $Ba(C_7H_4BrO_3)_2 \cdot H_2O$.	I.	Found. II.	III.
H_2O	3.07	3.21	3.21	...
Ba	23.34	23.42

I. 0.5258 gram of the salt dried at 100° gave 0.2149 gram $BaSO_4$.

II. 0.4787 gram of the salt dried at 100° gave 0.1955 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_7\text{H}_4\text{BrO}_3)_2$.	Found.	
		I.	II.
Ba	24.07	24.02	24.01

Calcic Bromfurfuracrylate, $\text{Ca}(\text{C}_7\text{H}_4\text{BrO}_3)_2 \cdot 3\text{H}_2\text{O}$.—This salt crystallises in columnar aggregations of plates, and is sparingly soluble in cold water, more readily in hot water. The air-dried salt effloresces over sulphuric acid, and is gradually decomposed at 100° , but may be dried without difficulty at 80° – 85° .

I. 1.1639 gram of the air-dried salt lost at 82° 0.1184 gram H_2O .

II. 0.7362 gram of the air-dried salt lost at 83° – 85° 0.0740 gram H_2O .

III. 0.6331 gram of the air-dried salt gave 0.1648 gram CaSO_4 .

IV. 0.5287 gram of the air-dried salt gave 0.1375 gram CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_7\text{H}_4\text{BrO}_3)_2 \cdot 3\text{H}_2\text{O}$.	Found.			
		I.	II.	III.	IV.
H_2O	10.07	10.17	10.05
Ca	7.61	7.65	7.65

0.6123 gram of the salt dried at 82° gave 0.1774 gram CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_7\text{H}_4\text{BrO}_3)_2$.	Found.
Ca	8.47	8.52

Sodic Bromfurfuracrylate, $\text{NaC}_7\text{H}_4\text{BrO}_3$.—This salt is readily soluble even in cold water, and crystallises in anhydrous nodular aggregations.

I. 0.7612 gram of the salt gave 0.2228 gram Na_2SO_4 .

II. 0.7589 gram of the salt gave 0.2206 Na_2SO_4 .

	Calculated for $\text{NaC}_7\text{H}_4\text{BrO}_3$.	Found.	
		I.	II.
Na	9.62	9.48	9.42

Argentie Bromfurfuracrylate, $\text{AgC}_7\text{H}_4\text{BrO}_3$.—The silver salt, formed by the addition of argentic nitrate to a neutral solution of the ammonium salt, proved to be nearly insoluble in water, and was apparently amorphous.

I. 0.3919 gram salt gave 0.2261 gram AgBr .

II. 0.4065 gram of the salt gave 0.2347 gram AgBr .

	Calculated for $\text{AgC}_7\text{H}_4\text{BrO}_3$.	Found.	
		I.	II.
Ag	33.34	33.13	33.16

Ethyl Bromfurfuracrylate, $C_7H_5BrO_3.C_2H_5$.—To a solution of the acid (5 parts) in somewhat more than its own weight of absolute alcohol (6.5 parts) was added concentrated sulphuric acid (3 parts), and the mixture heated upon the water-bath for two or three hours. We found that too long heating should be avoided, since decomposition then ensued, and a product was formed which undoubtedly was analogous to that obtained by Markwald.¹ We have, however, made no careful study of it. As soon as the etherification appeared to be complete, the ether was precipitated with water, dried with calcic chloride, and distilled under diminished pressure. The greater part of the product distilled at 151° – 152° under a pressure of 14 mm., and on cooling this distillate completely solidified. From ligroin the ether could be obtained in large flat prisms, which melted at 42° . It was readily soluble in alcohol, ether, chloroform, benzol, or ligroin, and had a faint aromatic odor.

I. 0.1968 gram substance gave 0.3168 gram CO_2 and 0.0673 gram H_2O .

II. 0.2251 gram substance gave 0.1722 gram AgBr.

III. 0.2545 gram substance gave 0.1943 gram AgBr.

	Calculated for $C_9H_5BrO_3$.	I.	Found. II.	III.
C	44.08	43.88
H	3.67	3.80
Br	32.65	...	32.55	32.49

We further attempted to make the amide, but found that the ether was hardly attacked by concentrated ammoniac hydrate at 100° , and that at a much higher temperature (215°) most of the ether employed also remained unchanged.

BROMFURFURBROMACRYLIC ACID.

It already has been mentioned that bromfurfurdibrompropionic acid is decomposed by heat with the evolution of hydrobromic acid, and the simultaneous formation of a disubstituted furfuracrylic acid might be inferred. We have made many attempts to bring about this loss of one molecule of hydrobromic acid by more convenient and more economical methods, but without success. In alcoholic solution potassic hydrate gave chiefly the ethylen derivative and potassic carbonate, no matter how the con-

¹ Loc. cit.

ditions of the reaction were varied. A number of high boiling neutral solvents gave no better results than those obtained by heating the acid by itself. The bromfurfurdibrompropionic acid was therefore carefully heated in shallow crystallising dishes immersed in a sulphuric acid bath. The hydrobromic acid thus escaped without blackening the product to any great extent. The temperature was slowly raised to 130° , and when at this point the formation of hydrobromic acid was no longer noticeable, the residue was boiled with dilute ammoniac hydrate filtered, heated with bone-black, and the filtered solution concentrated by evaporation. In this way sparingly soluble finely felted needles of ammoniac bromfurfurbromacrylate were obtained, which yielded the acid in a state of purity.

I. 0.2246 gram substance gave 0.2328 gram CO_2 and 0.0317 gram H_2O .

II. 0.2290 gram substance gave 0.2373 gram CO_2 and 0.0314 gram H_2O .

III. 0.2059 gram substance gave 0.2615 gram AgBr.

IV. 0.2025 gram substance gave 0.2571 gram AgBr.

	Calculated for $\text{C}_7\text{H}_4\text{Br}_2\text{O}_3$.	Found.			
		I.	II.	III.	IV.
C	28.38	28.27	28.26
H	1.35	1.57	1.53
Br	54.05	54.04	54.03

Bromfurfurbromacrylic acid is almost insoluble even in hot water. It dissolves freely in ether or alcohol, and when precipitated by water from a hot alcoholic solution is obtained in fine clustered needles. At ordinary temperatures it is very sparingly soluble in chloroform or carbonic disulphide, but dissolves somewhat more freely on heating. The acid melts at 178° – 179° , and small quantities of it may easily be sublimed without essential decomposition.

In spite of many attempts, we have been unable to obtain experimental evidence as to the position of the bromine atoms. We have also been unable to prepare definite products by the addition of bromine to the acid, or to form from it bromfurfurpropionic by the elimination of hydrobromic acid. The following salts may serve for the better characterisation of the acid.

Baric Bromfurfurbromacrylate, $\text{Ba}(\text{C}_7\text{H}_3\text{Br}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$.—This salt was prepared by adding baric chloride to a solution of the

ammonium salt. It is very sparingly soluble even in boiling water, and crystallises in lustrous scales. The air-dried salt contains two molecules of water, which it does not lose over sulphuric acid.

I. 1.4911 gram of the air-dried salt lost at 120° 0.0674 gram H_2O .

II. 0.8824 gram of the air-dried salt lost at 120° 0.0399 gram H_2O .

H_2O	Calculated for $Ba(C_7H_3Br_2O_3)_2 \cdot 2H_2O$.	Found.	
		I.	II.
	4.72	4.52	4.52

I. 0.2130 gram of the anhydrous salt gave 0.0684 gram $BaSO_4$.

II. 0.2229 gram of the anhydrous salt gave 0.0712 gram $BaSO_4$.

III. 0.4376 gram of the anhydrous salt gave 0.1398 gram $BaSO_4$.

Ba	Calculated for $Ba(C_7H_3Br_2O_3)_2$.	I.	Found.	
			II.	III.
	18.85	18.88	18.78	18.78

Argentio Bromfurfurbromacrylate, $AgC_7H_3Br_2O_3$.—The silver salt made by precipitation is very sparingly soluble even in boiling water, and is apparently amorphous.

I. 0.2052 gram of the salt dried over sulphuric acid gave 0.0951 gram $AgBr$.

II. 0.2101 gram of the salt dried over sulphuric acid gave 0.0977 gram $AgBr$.

Ag	Calculated for $AgC_7H_3Br_2O_3$.	Found.	
		I.	II.
	26.80	26.62	26.71

Potassic Bromfurfurbromacrylate, $KC_7H_3Br_2O_3$.—The potassium salt is sparingly soluble in cold water, more readily soluble in hot water, and crystallises in slender clustered needles which are anhydrous.

I. 0.2275 gram of the salt gave 0.0589 gram K_2SO_4 .

II. 0.5386 gram of the salt gave 0.1407 gram K_2SO_4 .

K	Calculated for $KC_7H_3Br_2O_3$.	Found.	
		I.	II.
	11.70	11.62	11.72

Ethyl Bromfurfurbromacrylate, $C_7H_3Br_2O_3 \cdot C_2H_5$.—The ethyl ether was made by heating for three hours on the water-bath a solution of the acid (4 parts) in absolute alcohol (40 parts), with the addition of a small amount (3 parts) of concentrated sulphuric

acid. The ether was then precipitated with water, washed with a dilute solution of sodic carbonate, and recrystallised from ligroin. It crystallised easily in radiated needles which melted at 55° – 56° and dissolved readily in alcohol, ether, chloroform, benzol, ligroin, or carbonic disulphide.

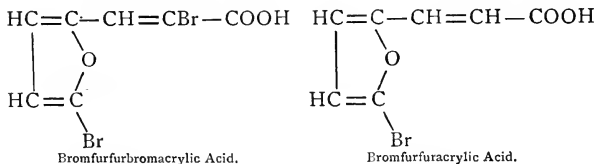
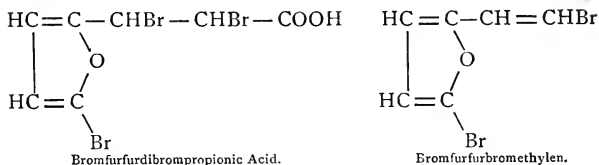
I. 0.3774 gram of substance gave 0.4592 gram CO_2 and 0.0849 gram H_2O .

II. 0.2125 gram substance gave 0.2464 gram AgBr.

III. 0.2179 gram substance gave 0.2525 gram AgBr.

	Calculated for $\text{C}_9\text{H}_6\text{Br}_2\text{O}_3$.	I.	Found. II.	III.
C	33.34	33.19
H	2.47	2.50
Br	49.39	...	49.35	49.32

While we have been unable to establish with precision the constitution of the foregoing derivatives of furfuracrylic acid, the analogies offered by the derivatives of pyromucic and cinnamic acids naturally suggest the following formulae for the substances in question:



LXXI.—ON THE SO-CALLED DIOXYMALEIC ACID.

BY W. S. HENDRIXSON.

Several years ago Bourgoin¹ announced the discovery of two new acids which he had obtained by replacing the bromine of brom-

¹ Bull. Soc. Chim. **19**, 482; **22**, 443.

maleic and dibrommaleic acid by hydroxyl, and which he therefore called oxymaleic and dioxymaleic acid. Although the experimental evidence as to the existence of these acids was very slight, and their assumed structure wholly anomalous, they soon found place in many text-books.

In 1886, at the suggestion of Fittig, the work of Bourgoin upon oxymaleic acid was repeated by Scherks,¹ who found that his statements were without foundation, and that brommaleic acid in aqueous solution was not in the least attacked by argentic oxide, even at 100°. Scherks further concluded that Bourgoin's statements concerning his dioxymaleic acid must also be incorrect, because the dibrommaleic acid which he used he claimed to have made from his tribromsuccinic acid, an acid which could not be formed under the given conditions, as shown by Fittig and Petri,² or if formed, would at once be decomposed into dibromacrylic acid and carbonic dioxide. This conclusion of Scherks seems hardly justified by Bourgoin's statements. The dibrommaleic acid which he used undoubtedly was made by the action of aqueous bromine upon succinic acid, and, while his material may have been far from pure, the question of its identity is in no way affected by his erroneous assumption that it had been formed by the decomposition of tribromsuccinic acid. In any case the subject seemed to demand a more careful investigation. At the suggestion of Prof. H. B. Hill, I have, therefore, repeated Bourgoin's work upon dioxymaleic acid, and find that decomposition is in this case readily effected, but that the product formed is not dioxymaleic acid.

The dibrommaleic acid needed for this investigation was made by the oxidation of mucobromic acid with cold fuming nitric acid, a method which had already been found in this laboratory to be much more advantageous than the methods previously described. Mucobromic acid was dissolved in cold fuming nitric acid, and the nearly saturated solution allowed to stand for several days at ordinary temperatures. When the mixture had completely solidified, the nitric acid was expelled by gentle heat, and the dry residue distilled from a small retort. In order to obtain a perfectly pure product, the distillate was dissolved in water, neutralised with baric carbonate, and the baric dibrommaleate precipitated by the addition of alcohol. The barium salt was then con-

¹ Ann. Chem. (Liebig) **207**, 223.

² Ibid. **195**, 70.

verted into the sodium salt, and from this the silver salt was made by precipitation with argentic nitrate.

According to Bourgoin, dioxymaleic acid is formed by heating argentic dibrommaleate with water to 150° . On opening the tubes after heating for five hours he found that carbonic dioxide escaped, that argentic bromide had been formed, and that the liquid in the tubes was distinctly acid. On the addition of argentic nitrate to this acid solution carefully neutralised with ammoniac hydrate he obtained a white insoluble silver salt, which gave on ignition a residue closely agreeing with the weight of metallic silver required by the formula $\text{Ag}_2\text{C}_4\text{H}_2\text{O}_6$. He found the acid to be a white crystalline solid, which was readily soluble in water and alcohol, and barely soluble in ether. With the alkalis and alkaline earths it formed readily soluble salts, and showed itself to be non-saturated in that it was capable of fixing hydrogen and bromine. Bourgoin gives, however, no analytical results whatsoever except the one already mentioned.

On following closely the directions of Bourgoin, I found that the argentic dibrommaleate had been almost completely decomposed, and that at least 95 per cent. of the theoretical amount of argentic bromide had been formed. The liquid in the tubes was strongly acid, but the carbonic dioxide which escaped was by no means insignificant in quantity. Although the aqueous solution gave a crystalline precipitate with argentic nitrate after careful neutralisation with ammoniac hydrate, it was thought advisable to distill the liquid with steam before preparing salts for analysis, since it was found that the acid volatilised readily under these conditions. The acid distillate was neutralised with calcic carbonate, the silver salt precipitated by the addition of argentic nitrate to the concentrated solution, and recrystallised from hot water. The silver salt thus obtained closely resembled argentic acetate, and its identity was established by analysis.

I. 0.4677 gram of the air-dried salt gave 0.5249 gram AgBr .

II. 0.2263 gram of the air-dried salt gave 0.1465 gram Ag .

III. 0.2056 gram of the salt dried over sulphuric acid gave 0.1082 gram CO_2 , 0.0330 gram H_2O , and 0.1327 gram Ag .

	Calculated for $\text{AgC}_2\text{H}_3\text{O}_2$.	I.	Found. II.	III.
Ag	64.67	64.46	64.73	64.54
C	14.37	14.35
H	1.80	1.78

The barium salt was also made by neutralising the acid distillate with baric carbonate. The salt obtained on evaporation was either recrystallised from water, or precipitated from a concentrated aqueous solution by alcohol. I failed to find any definite statements as to the composition of the salt thus precipitated by alcohol, but experiments of my own showed that it contained one molecule of water like the salt crystallised from water.

I. 1.1456 gram of the air-dried salt lost at 150° 0.0780 gram H₂O.

II. 0.9187 gram of the air-dried salt lost at 125° 0.0609 gram H₂O.

III. 0.4561 gram of the air-dried salt gave 0.3899 gram BaSO₄.

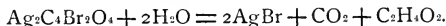
IV. 0.6868 gram of the air-dried salt gave 0.5841 gram BaSO₄.

	Calculated for Ba(C ₂ H ₃ O ₂) ₂ .H ₂ O.	I.	II.	Found.	III.	IV.
H ₂ O	6.59	6.80	6.62
Ba	50.18	50.25	50.02	

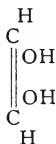
0.8554 gram of the salt dried at 125° gave 0.7811 gram BaSO₄.

	Calculated for Ba(C ₂ H ₃ O ₂) ₂ .	Found.
Ba	53.73	53.69.

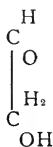
It thus appears that acetic acid is formed in the decomposition of argentic dibrommaleate by water at 150° and the reaction may be expressed by the equation:



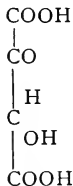
The weight of baric acetate which was obtained from the distilled liquid amounted to about 60 per cent. of the theoretical yield required by this equation, while 85 per cent. of the theoretical amount of free acid, calculated as acetic acid, was found by direct titration of the contents of the tubes. The higher result in the latter case may in part have been due to incomplete expulsion of the carbonic dioxide, but the most careful search failed to show that any well defined organic acid except acetic acid had been formed in the reaction. Dibrommaleic acid therefore yields, under the conditions prescribed by Bourgoin for its conversion into dioxymaleic acid, carbonic dioxide and acetic acid. The facts observed give no certain information as to the mechanism of the reaction. If it is assumed that the body



is first formed, it would pass at once into the aldehyde alcohol,



from which acetic acid would then be formed, precisely in the same way that tartronic acid is formed from dibrompyruvic acid,¹ or from dioxytartaric acid.² It is more probable, however, that the ketone acid



is the first product, and that this passes into acetic acid in a similar way through the loss of carbonic dioxide.

THE ELECTROLYSIS OF METALLIC PHOSPHATES IN ACID SOLUTION.

BY EDGAR F. SMITH.

Some experiments on the action of the current upon metallic phosphates have been published by Moore,³ and more recently Brand⁴ has communicated his experience with the pyrophosphates

¹ Grimaux, Bull. Soc. Chim. **27**, 440.

² Kékulé, Ann. Chem. (Liebig) **221**, 230.

³ Chem. News **53**, 209.

⁴ Zeit. für anal. Chem. **28**, 581.

dissolved in an excess of sodium pyrophosphate and also in ammonium hydroxide or carbonate. The experiments in this paper relate wholly to the deposition of metals from the solutions of their phosphates in normal phosphoric acid. The course pursued in the preparation of the solutions for electrolysis was to first precipitate the metals with an excess of disodium phosphate, dissolving the compound obtained in a measured volume of free phosphoric acid (sp. gr. 1.347), and then exposing this liquid to the action of currents of known strength. When operating upon mercuric solutions, prepared in the manner indicated, the deposition of the metal in the early part of the experiment was perfectly satisfactory, but as the decomposition advanced, a heavy white precipitate appeared in the solution, and, although it gradually suffered reduction, the metal that separated was so fluid-like that it mechanically carried down impurities, hence was unfit for electrolytic determinations, and the experiments in this direction were consequently suspended. Mercurous phosphate proved to be insoluble, or nearly so, in phosphoric acid. This is also the case with bismuth and lead phosphates, therefore neither of these metals was available in the proposed experiments.

Copper.

To a solution containing 0.0996 gram metallic copper, as sulphate, 10 cc. Na_2HPO_4 (sp. gr. 1.0358) and $3\frac{1}{2}$ cc. H_3PO_4 (sp. gr. 1.347) were added. The precipitated copper phosphate dissolved in $\frac{1}{2}$ cc. of acid, so that the deposition of metal occurred in the presence of 3 cc. of free phosphoric acid. The total dilution with water amounted to 125 cc. The current employed gave 0.15 cc. oxyhydrogen gas per minute. The copper deposit weighed 0.0997 gram. The metal precipitation was allowed to continue through the night. Later, two additional experiments were arranged in every respect similar to the one just described, increasing the current, however, to 0.5 cc. oxyhydrogen gas per minute. The copper found was in (a) 0.0990 gram, and in (b) 0.0994 gram. The addition of an excess of ammonium hydroxide to the filtrates did not produce the slightest blue coloration. The metallic copper from the above experiments showed a rich red color. The metallic lustre observed upon the metal deposited from solutions containing other free acids, *e. g.* HNO_3 , was not noticed here. That the conditions of the preceding depositions will answer for the separation of copper from other metals is evident from the results

recorded below. Strong currents deposit metallic iron and other metals from their phosphates in phosphoric acid solution, while they are unaffected by the feebler currents.

Copper from Iron.

A solution containing 0.0996 gram metallic copper, 0.1700 gram metallic iron, 30 cc. Na_2HPO_4 (sp. gr. 1.0358), and $4\frac{1}{2}$ cc. H_3PO_4 (sp. gr. 1.347), were diluted to 125 cc. with water and exposed to the action of a current generating 0.6 cc. oxyhydrogen gas per minute. The deposited copper weighed 0.0996 gram. Additional experiments verified this result. The filtrates contained no copper.

Copper from Aluminium.

Here the quantity of copper was the same as before, while the aluminium metal was 0.1000 gram, 20 cc. Na_2HPO_4 (sp. gr. 1.0358) with 3 cc. H_3PO_4 (sp. gr. 1.347). The total dilution was 100 cc. The current gave 0.3 cc. oxyhydrogen gas per minute. The copper deposited weighed 0.0995 gram.

Copper from Chromium.

Both metals were added as sulphates, the quantity of metallic chromium being in excess of that of the copper. The volume of alkaline phosphate was 20 cc., and that of the phosphoric acid 3 cc. The final dilution and current strength were the same as in the separation of copper from aluminium. The deposition was made during the night. The metal obtained equaled 0.0994 gram. It was brilliant red in color, similar to that noticed frequently by chemists in the separation of these two metals from each other. The chromium was oxidised to chromic acid. The filtrate gave no indication of unprecipitated copper. A duplicate experiment afforded a similar result.

Copper from Zinc.

In this separation there were present 0.1500 gram metallic zinc and alkaline phosphate and free phosphoric acid in the same quantities as with aluminium and chromium. The dilution was 100 cc. while the current gave but 0.15 cc. oxyhydrogen gas per minute. The deposited copper weighed 0.0993 gram. The filtrate gave no coloration upon the addition of an excess of ammonium hydroxide.

Copper from Cobalt.

With 0.0968 gram cobalt and conditions similar to those just given under copper and zinc, except that the current had increased to 0.22 cc. oxyhydrogen gas per minute, the deposited metal was found to be 0.0995 gram.

Copper from Nickel.

The nickel (0.1105 gram) was present as chloride, while the conditions of experiment were similar to those in the preceding example. The deposit of copper weighed 0.0996 gram.

In all of the experiments given above the copper deposited rapidly from the cold solutions. Before interrupting the current the acid liquid was siphoned off and replaced by water. The deposits were washed with cold and hot water. Alcohol and ether were not used. The drying was done upon a warm iron plate. The current employed was obtained from ten ordinary "crowfoot" cells. In each experiment the poles of the battery were about $\frac{3}{4}$ inch apart.

Cadmium.

As this metal deposits from solutions containing free sulphuric acid,¹ it was expected that the same would occur in the presence of free phosphoric acid. This is proved by the following experiments: 10 cc. cadmium sulphate (\equiv 0.1827 gram Cd) were precipitated by an excess of Na_2HPO_4 (sp. gr. 1.0358) and the phosphate dissolved in $1\frac{1}{2}$ cc. H_3PO_4 (sp. gr. \equiv 1.347). Total dilution 100 cc. The current gave 0.6 cc. oxyhydrogen gas per minute. Two determinations were made in this way. The found metal was in (a) 0.1839 gram and in (b) 0.1820 gram. The (a) deposit showed a little sponginess, and this doubtless caused it to give a higher result than required by the theory. The filtrates from these deposits gave no cadmium reactions upon applying the usual tests for that metal. In two other determinations where the only change made in the conditions of experiment was the reduction of the current to 0.40 cc. gas per minute, the deposited cadmium weighed in (a) 0.1828 gram and in (b) 0.1833 gram. These figures indicate complete deposition and that the method is reliable. Cadmium does not, however, deposit as rapidly as copper under like circumstances. It was also found advisable

¹ This Journal 2, 41.

towards the close of the experiment to increase the current strength. The acid liquid should always be removed from the dish in which the deposition occurs before the current is finally interrupted. The deposits were washed and dried as described with copper.

Cadmium from Zinc.

0.1827 gram cadmium and 0.1500 gram zinc (both as sulphates) were precipitated by 40 cc. disodium phosphate, dissolved in 3 cc. H_3PO_4 (sp. gr. 1.347), and acted upon in the cold for twelve hours with a current giving 0.35 cc. oxyhydrogen gas per minute. The cadmium deposit weighed 0.1820 gram. The entire dilution was 125 cc. With a second cadmium solution ($= 0.1057$ gram Cd), together with the same quantity of zinc as before, 20 cc. Na_2HPO_4 (sp. gr. 1.0358), 3 cc. H_3PO_4 (sp. gr. $= 1.347$), and 100 cc. water, 0.1060 gram cadmium was obtained. This deposit was crystalline, but in spots slightly spongy, which may account for its being somewhat higher than the theoretical. Two more separations of these metals were made, with a reduction of the phosphoric acid from 3 cc. to 2 cc., otherwise the conditions remained as before, and the cadmium obtained was in (a) 0.1057 gram and in (b) 0.1051 gram. The current strength in these depositions was 0.37 cc. oxyhydrogen gas per minute in each dish. *b* is low; its filtrate gave a trace of cadmium sulphide upon testing with hydrogen sulphide. My experience has been that in experiments such as these it should never be omitted to increase the current for about one hour previous to the final disconnection.

Cadmium from Nickel.

Only two experiments were made with these metals. They were conducted in the same manner as those with zinc and cadmium. The cadmium found was in (a) 0.1059 gram and in (b) 0.1051.

Cadmium from Iron.

The quantities of the metals were 0.1700 gram iron and 0.1057 gram cadmium. The alkaline phosphate and phosphoric acid were the same as with cadmium and zinc. Total dilution 100 cc. Current 0.37 cc. oxyhydrogen gas per minute. The deposited cadmium weighed in (a) 0.1058 gram and in (b) 0.1062 gram.

Cadmium from Chromium.

In this separation the conditions were the same as with the preceding metals. Found cadmium was 0.1055 gram. The deposit was spongy, and the reduction of the strength of the current seemed not to remove this undesirable feature.

Cadmium from Aluminium.

The quantity of cadmium present was 0.2120 gram, while the aluminium was in equal amount. The alkaline phosphate, free phosphoric acid, total dilution, and current strength were the same as with zinc and iron. The results obtained were in (a) 0.2122 gram Cd and in (b) 0.2120 gram Cd.

The separation of copper from the metals mentioned in connection with it was not attended by any difficulty whatever, but with cadmium compliance with the conditions mentioned was absolutely required, otherwise the results varied. In solutions containing free phosphoric acid, cadmium is unusually inclined to sponginess, so that concentration of liquid should be avoided, and the poles of the acting battery should not approach too closely to each other. The most favorable separation was found to be 1½ inches and the proper dilution of the liquid 100–150 cc. Such, at least, was the case in the separations just described.

Copper from Cadmium.

These metals have been separated from each other in the presence of free nitric acid,¹ and also in the presence of free sulphuric acid.² From the results about to be given, their separation in the presence of free phosphoric acid is also possible. Two experiments were conducted under the following conditions: 0.2452 gram copper as sulphate, 0.1827 gram cadmium as sulphate, 20 cc. Na_2HPO_4 (sp. gr. 1.0358), and 10 cc. H_3PO_4 (sp. gr. = 1.347), with a total dilution of 125 cc., were exposed to the action of a current generating 0.10 cc. oxyhydrogen gas per minute for a period of twelve hours, when the following amounts of metallic copper were obtained: in (a) 0.2451 gram and in (b) 0.2452 gram. In a third experiment, with double the amount of copper present, the current was allowed to act through the night, and the deposited metal weighed 0.4904 gram. Again, with a current liberating 0.2 cc. oxyhydrogen gas per minute, conditions in all other

¹ This Journal 2, 42.

² Ibid. 12, 110.

respects similar to those previously mentioned, the found copper was 0.2451 gram. Cadmium was not detected in these deposits. The filtrates showed no trace of copper.

Silver phosphate is readily dissolved by phosphoric acid, but from such solutions even the feeblest currents deposit the metal in a spongy condition, so that it was useless in the quantitative work. But from an ammoniacal solution of the phosphate the deposition of silver metal is quite rapid and satisfactory. Two experiments gave, with a current liberating 0.20 cc. oxyhydrogen gas per minute, in (a) 0.1065 gram and in (b) 0.1061 gram Ag, the required being 0.1062 gram. Ammonia just sufficient to dissolve the phosphate is all that should be used. As I have not observed this mode of depositing silver described in the literature of electrolysis, I include it here, although it is only to the deportment of acid phosphate solutions that I wish to direct attention. The behavior of lead phosphate in alkaline solution has been recorded by me.¹ The results given are quite satisfactory. As already remarked, its phosphate being insoluble in phosphoric acid excludes experimentation in that direction.

One of the most interesting observations made in this study of acid phosphates and the electric current is that with manganese. It is well known that from nitric or sulphuric acid solution this metal is deposited as dioxide by the current. In the presence of phosphoric acid, where there is a decided excess of the latter, the deposition of dioxide upon the positive pole does not take place. This behavior has enabled me to present the following separations of copper from manganese :

1. 0.1770 gram copper as sulphate, 0.1500 gram manganese as sulphate, 30 cc. Na_2HPO_4 (sp. gr. 1.0358), 10 cc. H_3PO_4 (sp. gr. 1.347), with a total dilution of 120 cc., were exposed to the action of a current giving 1 cc. oxyhydrogen gas per minute. Copper found equaled 0.1765 gram.

2. The conditions the same as in (1), except that the current gave 1.4 cc. oxyhydrogen gas per minute. Found copper weighed 0.1770 gram. The positive pole showed no dioxide deposition. When the current exceeded that given in (1) and (2) a pink coloration was observed about the anode. This non-precipitation of the manganese is very likely due to the formation of

¹ Proceedings Am. Phil. Soc., 1887.

the phosphate of the sesquioxide, which is only decomposed, and then but partially, by much more powerful currents than were used in this separation.

The behavior of other metallic phosphates in acid solution is receiving attention in this laboratory.

UNIV. OF PENNA., PHILA., PA., *March 28, 1890.*

A METHOD FOR THE ESTIMATION OF ALBUMEN IN URINE.

BY T. C. VAN NÜYS AND R. E. LYONS.

That albuminous bodies are completely precipitated from solution by tannic acid is proven by the investigations of Liborius,¹ Girgensohn,² Sebelien³ and others. By Sebelien's method of estimating the total quantity of albuminous bodies in milk, 3 to 5 grams milk is diluted with some water, a few drops of a solution of sodium chloride or magnesium sulphate added, and the fluid is then treated with an excess of Almén's solution of tannic acid,⁴ the precipitate filtered off, well washed, and the nitrogen in the precipitate estimated by Kjeldahl's method.

The weight of nitrogen is multiplied by 6.37, the product of which is the weight of albuminous bodies in the weight of the milk taken. The factor 6.37 is the number of times the per cent. (15.7) of the nitrogen in albumen is contained in 100 ($\frac{100}{15.7} = 6.37$).

Sebelien's method differs from the methods of Almén and Liborius in not depending on the fixed constitution of the compound of albumen and tannic acid, but rather all of the albumen is separated from solution, and that all nitrogen compounds not albuminous can be removed from the precipitate by washing.

Our studies of this subject were carried on with the view of

¹ Beitrag zu quant. Eiweissbestimmungen. Dorpat, 1871.

² Beiträge zur Albuminometrie. Dorpat, 1872.

³ Studien über die analyt. Bestimmungsweise der Eiweisskörper mit besonderer Rücksicht auf die Milch.

⁴ 4 grams tannic acid, 8 cc. acetic acid (1 part glacial acetic acid and 3 parts water), 190 cc. dilute alcohol, 50 per cent.

ascertaining if a method of estimating albuminous bodies in urine, employing tannic acid, is practical. As urine contains nitrogenous compounds in considerable quantities, the tannic acid compound of albumen is not easily washed until pure; besides, by continued contact of an acid, or acid salts, uric acid is precipitated, which would remain in part with the albumen; and as the volumetric method of estimating albumen with tannic acid has not been found accurate,¹ if there remains a practical method for estimating albumen in urine with tannic acid, it is that the total quantity of nitrogen in albuminous urine is first estimated, following which estimation is made of the quantity of nitrogen in the urine having its albumen separated by means of tannic acid. The difference in the quantities of nitrogen found is the weight of nitrogen of the albumen, which, multiplied by 6.37, would give the weight of albumen. To determine if the method here outlined yields accurate results, the question arises if uric acid or other nitrogenous compounds of normal urine are retained by the precipitate formed by the tannic acid and albumen when filtered, so that the volume of urine in the undiluted filtrate would contain a smaller quantity of the normal nitrogenous constituents of the urine than is in a corresponding volume of urine before the separation of albumen.

To determine this we estimated the nitrogen in normal urine before and after the introduction and removal of known quantities of albumen. We determined if Almén's solution of tannic acid produces a separation of any part of the nitrogenous compounds of normal urine, or of urine containing an abnormal quantity of the urates, and finally we employed the new method and the gravimetric method in estimating the albumen in urine and compared the results.

Pure albumen was prepared by dissolving the whites of eggs in a small quantity of water, saturating the solution with magnesium sulphate and filtering. The filtrate was then treated with dilute acetic acid until a precipitate ceased to form, filtered off, and the precipitate washed with a saturated solution of magnesium sulphate.

Having pressed the precipitate between porous paper, it was dissolved in a small quantity of water, the solution neutralised with sodium hydrate, and dialysed until nearly all of the magne-

¹ Beiträge zur Albuminometrie von Girgensohn; Dorpat, 1872. Einige Methode zur Werthbestimmungen der Milch von Taraszewicz; Dorpat, 1873.

sium sulphate was separated. To the turbid solution of albumen a small quantity of the oil of thyme was added to prevent bacterial decomposition, and having mixed well, the solution was filtered. In case a solution was too dilute it was concentrated by evaporation at 40° to 50° C., and when nearly free of ash, some sodium chloride was added to facilitate the precipitation with tannic acid. Solutions of ovalbumen we number 1, 2, 3, etc.

FIRST ALBUMEN SOLUTION.

Estimation of Albumen.

(1). 10 cc. albumen solution, 10 cc. water, mixed.

(a). 5 cc. of the solution required by Kjeldahl's method 47.3 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the solution required by Kjeldahl's method 47.3 cc. $\frac{1}{5}$ normal KOH, corresponding to 0.1512 gram nitrogen in 100 cc. of the undiluted solution of albumen.

(2). 10 cc. albumen solution, 10 cc. Almén's solution of tannic acid, mixed and filtered without dilution.

(a). 5 cc. of the filtrate required by Kjeldahl's method 49.9 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the filtrate required by Kjeldahl's method 49.95 cc. $\frac{1}{5}$ normal KOH, average 49.925 cc., corresponding to 0.0084 gram nitrogen of bodies not albuminous in 100 cc. of the albumen solution. The quantity of nitrogen of bodies not albuminous deducted from the total quantity of nitrogen, 0.1512 gram, leaves 0.1428 gram nitrogen of albumen, corresponding to 0.90963 gram albumen in 100 cc.

Urine.

(1). 10 cc. normal filtered urine, 10 cc. water, mixed.

(a). 5 cc. of the diluted urine required by Kjeldahl's method 35.8 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the diluted urine required by Kjeldahl's method 35.8 cc. $\frac{1}{5}$ normal KOH, corresponding to 1.5904 gram nitrogen in 100 cc. of the undiluted urine.

(2). 20 cc. urine, 10 cc. albumen solution, 10 cc. Almén's solution of tannic acid, mixed well in a small flask, and filtered without diluting.

(a). 5 cc. of the filtrate required by Kjeldahl's method 35.75 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the filtrate required by Kjeldahl's method 35.8 cc. $\frac{1}{5}$ normal KOH, average 35.77 cc., corresponding to 1.5932 gram nitrogen in 100 cc. of the undiluted urine; but as there was 0.0084 gram nitrogen in 100 cc. of the albumen solution which was not of the albumen and therefore not precipitated by tannic acid, and the volume of No. 2, 5 cc. is $\frac{1}{5}$ albumen solution, there is $\frac{1}{5}$ of 0.0084, 0.0021 gram nitrogen of bodies not albuminous of the urine, and consequently $1.5932 - 0.0021 = 1.5911$ gram nitrogen in 100 cc. urine. Therefore there was a gain of 0.0007 gram nitrogen by the process, $1.5911 - 1.5904 = 0.0007$.

SECOND ALBUMEN SOLUTION.

Estimation of Albumen.

(1). 10 cc. albumen solution, 10 cc. water.

(a). 5 cc. of the diluted solution required 47.9 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the diluted solution required 48.0 cc. $\frac{1}{5}$ normal KOH, average 47.95 cc., corresponding to 0.2296 gram nitrogen in 100 cc. of the undiluted albumen solution.

(2). 10 cc. albumen solution, 5 cc. Almén's solution, 5 cc. water, mixed well in a small flask and filtered.

(a). 5 cc. of the undiluted filtrate required 49.95 cc. $\frac{1}{5}$ normal KOH.

(b) 5 cc. of the undiluted filtrate required 49.95 cc. $\frac{1}{5}$ normal KOH, corresponding to 0.0056 gram nitrogen of bodies not albuminous in 100 cc. of the undiluted albumen solution. Deducting the latter weight from the weight of the total quantity of nitrogen ($0.2296 - 0.0056 = 0.224$), there is 0.224 gram nitrogen of the albumen in 100 cc. of the solution, which corresponds to 1.42688 gram albumen in 100 cc. ($0.224 \times 6.37 = 1.42688$).

Urine I.

(1). 10 cc. normal filtered urine, 10 cc. water.

(a). 5 cc. of the diluted urine required 37.3 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the diluted urine required 37.35 cc. $\frac{1}{5}$ normal KOH, average 37.325 cc., corresponding to 1.4196 gram nitrogen in 100 cc. of the undiluted urine.

(2). 10 cc. urine, 5 cc. Almén's solution, 5 cc. water, mixed well in a small flask and filtered.

(a). 5 cc. of the filtrate required 37.25 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the filtrate required 37.3 cc. $\frac{1}{5}$ normal KOH, average 37.275 cc., corresponding to 1.4252 gram nitrogen in 100 cc. undiluted urine.

Deducting $\frac{1}{4}$ of 0.0056 gram, the weight of nitrogen of bodies not albuminous, there remains 1.4238 gram nitrogen in 100 cc. of the undiluted urine. The results show a gain of 0.0042 gram nitrogen in 100 cc. of the undiluted urine after the separation of the albumen, $1.4238 - 1.4196 = 0.0042$.

Urine II.

(1). 10 cc. normal filtered urine, 10 cc. water.

(a). 5 cc. of the diluted urine required 35.0 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the diluted urine required 34.95 cc. $\frac{1}{5}$ normal KOH, average 34.975 cc., corresponding to 1.6828 gram nitrogen in 100 cc. of the undiluted urine.

(2). 10 cc. filtered urine, 5 cc. albumen solution, 5 cc. Almén's solution, mixed well in a small flask and filtered.

(a). 5 cc. of the filtrate required 34.9 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the filtrate required 35.0 cc. $\frac{1}{5}$ normal KOH, average 34.95 cc., corresponding to 1.6856 gram nitrogen in 100 cc. undiluted urine; and by deducting the weight of the nitrogen of bodies not albuminous in the solution, 0.0014, there remains 1.6842 gram nitrogen in 100 cc. of the undiluted urine. By the results obtained there was found 0.0014 gram more nitrogen in 100 cc. of the undiluted urine after the separation of the albumen than there was in the same volume of undiluted urine before the addition of albumen.

THIRD ALBUMEN SOLUTION.

Estimation of Albumen.

(1). 10 cc. albumen solution, 10 cc. water.

(a). 5 cc. of the diluted solution required 44.4 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the diluted solution required 44.35 cc. $\frac{1}{5}$ normal KOH, average 44.375 cc., corresponding to 0.63 gram nitrogen in 100 cc. of the undiluted solution.

(2). 10 cc. undiluted albumen solution, 10 cc. Almén's solution, mixed well and filtered. The filtrate was free of nitrogen.

0.63 gram nitrogen corresponds to 4.0131 grams albumen in 100 cc. of the solution.

Urine.

- (1). 10 cc. filtered normal urine, 10 cc. water.
 - (a). 5 cc. of the diluted urine, 38.7 cc. $\frac{1}{5}$ normal KOH.
 - (b). 5 cc. of the diluted urine, 38.8 cc. $\frac{1}{5}$ normal KOH.
 - (c). 5 cc. of the diluted urine, 38.75 cc. $\frac{1}{5}$ normal KOH, average 38.75 cc., corresponding to 1.26 gram nitrogen in 100 cc. of the undiluted urine.
- (2). 10 cc. normal filtered urine, 5 cc. albumen solution, 5 cc. Almén's solution, mixed well and filtered.
 - (a). 5 cc. of the filtrate required 38.8 cc. $\frac{1}{5}$ normal KOH.
 - (b). 5 cc. of the filtrate required 38.8 cc. $\frac{1}{5}$ normal KOH, corresponding to 1.2544 gram nitrogen in 100 cc. of the undiluted urine, or 0.0056 gram nitrogen less than in 100 cc. of the urine before the separation of albumen.

FOURTH ALBUMEN SOLUTION.

Estimation of Albumen.

- (1). 10 cc. albumen solution, 10 cc. water.
 - (a). 5 cc. of the solution required 48.9 cc. $\frac{1}{5}$ normal KOH.
 - (b). 5 cc. of the solution required 49.0 cc. $\frac{1}{5}$ normal KOH, average 48.95 cc., corresponding to 0.0588 gram nitrogen in 100 cc. of the undiluted solution.
- (2). 10 cc. albumen solution, 10 cc. Almén's solution, mixed well and filtered.

The filtrate was free of nitrogen. 0.0588 gram nitrogen corresponds to 0.3745 gram albumen in 100 cc. of the undiluted solution.

Urine.

- (1). 5 cc. normal filtered urine, 25 cc. water.
 - (a). 5 cc. of the diluted urine required 47.65 cc. $\frac{1}{5}$ normal KOH.
 - (b). 5 cc. of the diluted urine required 47.7 cc. $\frac{1}{5}$ normal KOH, average 47.675 cc., corresponding to 0.7812 gram nitrogen in 100 cc. of the undiluted urine.
- (2). 5 cc. urine, 20 cc. albumen solution, 5 cc. Almén's solution, mixed and filtered.
 - (a). 5 cc. of the filtrate required 47.7 cc. $\frac{1}{5}$ normal KOH.
 - (b). 5 cc. of the filtrate required 47.7 cc. $\frac{1}{5}$ normal KOH, corresponding to 0.7728 gram nitrogen in 100 cc. of the undiluted urine, therefore 0.0084 gram of nitrogen less than in 100 cc. of the urine before the separation of albumen.

FIFTH ALBUMEN SOLUTION.

Estimation of Albumen.

(1). 10 cc. albumen solution, 10 cc. water.

(a). 5 cc. of the solution required 49.55 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the solution required 49.6 cc. $\frac{1}{5}$ normal KOH, average 49.57 cc., corresponding to 0.04816 gram nitrogen in 100 cc. of the undiluted solution.

(2). 10 cc. albumen solution, 5 cc. Almén's solution, 5 cc. water, mixed and filtered.

The filtrate was free of nitrogen. 0.04816 gram nitrogen corresponds to 0.3067 gram albumen in 100 cc. of the undiluted solution.

Urine.

(1). 10 cc. normal filtered urine, 10 cc. water.

(a). 5 cc. of the diluted urine required 32.5 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the diluted urine required 32.45 cc. $\frac{1}{5}$ normal KOH, average 32.47 cc., corresponding to 1.9633 gram nitrogen in 100 cc. of the undiluted urine.

(2). 15 cc. urine, 9 cc. albumen solution, 6 cc. Almén's solution, mixed and filtered.

(a). 5 cc. of the filtrate required 32.5 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the filtrate required 32.5 cc. $\frac{1}{5}$ normal KOH, corresponding to 1.96 gram nitrogen in 100 cc. undiluted urine. Therefore there was found 0.0033 gram nitrogen less in 100 cc. of the urine after the addition and removal of the albumen, $1.9633 - 1.96 = 0.0033$.

SIXTH ALBUMEN SOLUTION.

Estimation of Albumen.

(1). 10 cc. albumen solution, 10 cc. water.

(a). 5 cc. of the diluted solution required 48.0 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the diluted solution required 48.05 cc. $\frac{1}{5}$ normal KOH, average 48.025 cc., corresponding to 0.2212 gram nitrogen in 100 cc. of the undiluted solution.

(2). 10 cc. albumen solution, 10 cc. Almén's solution, mixed and filtered. The filtrate was free of nitrogen.

0.2212 gram nitrogen corresponds to 1.4090 gram albumen in 100 cc. of the solution, $0.2212 \times 6.37 = 1.4090$.

Urine I.

(1). 20 cc. normal filtered urine, 20 cc. water.

(a). 5 cc. of the diluted urine required 38.1 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the diluted urine required 38.05 cc. $\frac{1}{5}$ normal KOH, average 38.07 cc., corresponding to 1.3361 gram nitrogen in 100 cc. of the undiluted urine.

(2). 20 cc. urine, 10 cc. albumen solution, 10 cc. Almén's solution, mixed and filtered.

(a). 5 cc. of the filtrate required 38.1 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the filtrate required 38.15 cc. $\frac{1}{5}$ normal KOH, average 38.125 cc., corresponding to 1.33 gram nitrogen in 100 cc. of the undiluted urine. Therefore there was found 0.0061 gram nitrogen less in 100 cc. of the urine after the addition and removal of the albumen, $1.3361 - 1.33 = 0.0061$.

Urine II.

(1). 20 cc. normal filtered urine, 20 cc. water.

(a). 5 cc. of the diluted urine required 40.45 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the diluted urine required 40.4 cc. $\frac{1}{5}$ normal KOH, average 40.425 cc., corresponding to 1.0724 gram nitrogen in 100 cc. of the undiluted urine.

(2). 20 cc. urine, 10 cc. albumen solution, 10 cc. Almén's solution, mixed and filtered.

(a). 5 cc. of the filtrate required 40.4 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the filtrate required 40.5 cc. $\frac{1}{5}$ normal KOH, average 40.45 cc., corresponding to 1.0696 gram nitrogen in 100 cc. of the undiluted urine. Therefore there was found 0.0028 gram nitrogen less in 100 cc. of the undiluted urine after the addition and removal of the albumen, $1.0724 - 1.0696 = 0.0028$.

SUMMARY OF RESULTS.

Albumen Solution.	Grams Albumen in 100 cc. of the Solution.	Total grams Nitrogen in 100 cc. of the Urine.	Dilution of the Urine.	Variation in quantity of Nitrogen in grams in 100 cc. of the Undiluted Urine before introduction of Albumen and after its removal.
I	0.9096	I.5904	I to 2	+ 0.0007
II	1.4268	I 1.4196	I to 2	+ 0.0042
II	1.4268	II 1.6828	I to 2	+ 0.0014
III	4.0131	1.2600	I to 2	- 0.0056
IV	0.3745	0.7812	I to 6	- 0.0084
V	0.3607	1.9633	I to 2	- 0.0033
VI	1.4090	I 1.3360	I to 2	- 0.0061
VI	1.4090	II 1.0724	I to 2	- 0.0028

In case the urine is diluted to a greater degree than 1 to 2, the limit of error in the estimated quantity of nitrogen increases as the quantity of nitrogen decreases by the dilution.

This is understood from the fact that with 5 cc. urine, 0.1 cc. of the $\frac{1}{5}$ normal KOH corresponds to 0.0056 gram nitrogen in 100 cc. of the urine; and if the urine be diluted from 1 to 2 or 1 to 4, 0.1 cc. $\frac{1}{5}$ normal KOH corresponds to 0.012 and 0.0224 gram nitrogen respectively. To determine if uric acid or other nitrogenous compound in normal, acid, or neutral urine, separates by contact with tannic acid, as in Almén's solution, in different periods of time, the following estimations were made.

NORMAL URINE I.

Estimation of Nitrogen.

(1). 10 cc. filtered urine, 10 cc. water.

(a). 5 cc. of the diluted urine required 47.25 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the diluted urine required 47.3 cc. $\frac{1}{5}$ normal KOH, average 47.275 cc., corresponding to 0.3052 gram nitrogen in 100 cc. of the undiluted urine.

(2). 10 cc. filtered urine, 10 cc. Almén's solution, mixed well in a small flask, let stand 15 minutes and filtered.

(a). 5 cc. of the filtrate required 47.3 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the filtrate required 47.25 cc. $\frac{1}{5}$ normal KOH, average 47.275 cc., corresponding to 0.3052 gram nitrogen in 100 cc. of the undiluted urine.

(3). 10 cc. filtered urine, 10 cc. Almén's solution, mixed well in a small flask, let stand 45 minutes, and filtered.

(a). 5 cc. of the filtrate required 47.2 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the filtrate required 47.2 cc. $\frac{1}{5}$ normal KOH, corresponding to 0.3136 gram nitrogen in 100 cc. of the undiluted urine.

(4). 10 cc. filtered urine, 10 cc. Almén's solution, mixed well in a flask, let stand 60 minutes and filtered.

(a). 5 cc. of the filtrate required 47.25 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the filtrate required 47.3 cc. $\frac{1}{5}$ normal KOH, average 47.275 cc., corresponding to 0.3052 gram nitrogen in 100 cc. of the undiluted urine.

From the results of these estimations it is seen that no nitrogen compound was separated from the urine by contact with the tannic acid solution, even when the time was extended to one hour, but the

urine in this case contained a minimum quantity of nitrogen, and it may be inferred that the urine contained a minimum quantity of uric acid.

NORMAL URINE II.

Urine was highly colored, acid in reaction, sp. gr. 1.031.

Estimation of Nitrogen.

(1). 10 cc. filtered urine, 10 cc. water.

(a). 5 cc. of the diluted urine required 31.95 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the diluted urine required 31.9 cc. $\frac{1}{5}$ normal KOH, average 31.925 cc., corresponding to 2.0244 grams nitrogen in 100 cc. of the undiluted urine.

(2). 10 cc. urine, 10 cc. Almén's solution, mixed well in a flask, let stand 20 minutes and filtered.

(a). 5 cc. of the filtrate required 31.8 cc. $\frac{1}{5}$ normal KOH, corresponding to 2.0384 grams nitrogen in 100 cc. of the undiluted urine.

(3). 10 cc. urine, 10 cc. Almén's solution, mixed well in a flask, let stand 45 minutes and filtered.

(a). 5 cc. of the filtrate required 32.0 cc. $\frac{1}{5}$ normal KOH, corresponding to 2.016 grams nitrogen in 100 cc. of the undiluted urine.

(4). 10 cc. urine, 10 cc. Almén's solution, mixed well in a flask, let stand 60 minutes and filtered.

(a). 5 cc. of the filtrate required 32.1 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the filtrate required 32.1 cc. $\frac{1}{5}$ normal KOH, corresponding to 2.0048 grams nitrogen in 100 cc. of the undiluted urine.

The increased quantity of nitrogen found in the urine after having stood with the tannic acid 20 minutes was due either to absorption of ammonia from the air of the laboratory or to an error in the titrations, probably from the latter, as but one estimation was made.

By contact with tannic acid 45 and 60 minutes, the losses of nitrogen were 0.0084 and 0.0196 gram respectively. As 0.075 cc. of the $\frac{1}{5}$ normal KOH corresponds to 0.0084 gram nitrogen when the dilution is 1 to 2, there is no evidence that any nitrogen compound, uric acid, was separated by the contact, but that there was a loss of nitrogen by the urine remaining in contact with tannic acid 60 minutes is probable.

In order to subject urine containing an abnormal quantity of uric acid, pure urate of potassium was dissolved in normal urine,

neutral in reaction; solution having taken place, the urine was filtered and the uric acid in the filtrate estimated. The quantity of uric acid in 100 cc. urine was 0.3575 gram, corresponding to about 6 grams uric acid eliminated in 24 hours.

Estimation of Nitrogen.

(1). 10 cc. of the filtered urine containing the potassium urate, 10 cc. water.

(a). 5 cc. of the diluted urine required 32.2 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the diluted urine required 32.2 cc. $\frac{1}{5}$ normal KOH, corresponding to 1.9801 gram nitrogen in 100 cc. of the undiluted urine.

(2). 10 cc. filtered urine, 10 cc. Almén's solution, mixed well in a small flask, let stand 20 minutes and filtered.

(a). 5 cc. of the filtrate required 32.4 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the filtrate required 32.45 cc. $\frac{1}{5}$ normal KOH, average 32.425 cc., corresponding to 1.9684 gram nitrogen in 100 cc. of the undiluted urine. The results of the estimations indicate the separation of 0.0117 gram nitrogen in 100 cc. of the urine by contact with the tannic acid.

Albumen was next estimated by this method, and also in the same urine by the gravimetric method.

ALBUMINOUS URINE I.

(1). 30 cc. filtered urine, 10 cc. water.

(a). 5 cc. of the diluted urine required 40.3 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the diluted urine required 40.35 cc. $\frac{1}{5}$ normal KOH.

(c). 5 cc. of the diluted urine required 40.25 cc. $\frac{1}{5}$ normal KOH, average 40.3 cc., corresponding to 0.72426 gram nitrogen in 100 cc. undiluted urine.

(2). 30 cc. filtered urine, 10 cc. Almén's solution, mixed well and filtered.

(a). 5 cc. of the filtrate required 41.1 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the filtrate required 41.2 cc. $\frac{1}{5}$ normal KOH.

(c). 5 cc. of the filtrate required 41.15 cc. $\frac{1}{5}$ normal KOH, average 41.15 cc., corresponding to 0.6608 gram nitrogen in 100 cc. of the undiluted urine. The difference in the quantities of nitrogen estimated in 1 and 2 is 0.06346 gram, corresponding to 0.40424 gram albumen in 100 cc. urine.

The Gravimetric Method.

The average of three estimations of albumen in 100 cc. of the urine was 0.4399 gram, hence the difference in the results of both methods is 0.0357 gram albumen in 100 cc.

: ALBUMINOUS URINE II.

(1). 10 cc. filtered urine, 10 cc. water.

(a). 5 cc. of the diluted urine required 40.9 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the diluted urine required 40.9 cc. $\frac{1}{5}$ normal KOH, corresponding to 1.0192 gram nitrogen in 100 cc. of the undiluted urine.

(2). 10 cc. filtered urine, 10 cc. Almén's solution, mixed well in a flask and filtered.

(a). 5 cc. of the filtrate required 40.95 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the filtrate required 41.0 cc. $\frac{1}{5}$ normal KOH, average 40.97 cc., corresponding to 1.01136 gram nitrogen in 100 cc. of the undiluted urine. The difference in the quantities of nitrogen in 100 cc. of the urine before and after the separation of albumen is 0.00784 gram, corresponding to 0.04994 gram albumen in 100 cc. urine.

The Gravimetric Method.

The average of two estimations of albumen in 100 cc. of the urine was 0.0506 gram, hence the difference in the results of both methods is 0.0006 gram.

ALBUMINOUS URINE III.

(1). 30 cc. of the filtered urine, 20 cc. water.

(a). 5 cc. of the diluted urine required 34.35 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the diluted urine required 34.3 cc. $\frac{1}{5}$ normal KOH, average 34.32 cc., corresponding to 1.4634 gram nitrogen in 100 cc. of the undiluted urine.

(2). 30 cc. filtered urine, 20 cc. Almén's solution, mixed and filtered.

(a). 5 cc. of the filtrate required 35.7 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the filtrate required 35.8 cc. $\frac{1}{5}$ normal KOH, average 35.75 cc., corresponding to 1.33 gram nitrogen in 100 cc. of the undiluted urine. The difference in the quantities of nitrogen in 100 cc. before and after the separation of albumen is 0.1334 gram, corresponding to 0.8497 gram albumen in 100 cc. of the urine.

The Gravimetric Method.

The average of three estimations of albumen by the gravimetric method was 0.8557 gram albumen in 100 cc. of the urine, hence the difference in results obtained by both methods is 0.006 gram albumen in 100 cc. of the urine.

ALBUMINOUS URINE IV.

(1). 20 cc. of the filtered urine, 10 cc. water.

(a). 5 cc. of the diluted urine required 35.75 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the diluted urine required 35.85 cc. $\frac{1}{5}$ normal KOH, average 35.8 cc., corresponding to 1.1928 gram nitrogen in 100 cc. of the undiluted urine.

(2). 20 cc. filtered urine, 10 cc. Almén's solution, mixed and filtered.

(a). 5 cc. of the filtrate required 36.1 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the filtrate required 36.1 cc. $\frac{1}{5}$ normal KOH, corresponding to 1.1676 gram nitrogen in 100 cc. of the undiluted urine. The difference in the quantities of nitrogen found before and after the removal of the albumen is 0.0252 gram, corresponding to 0.1605 gram albumen in 100 cc. of the urine.

The Gravimetric Method.

The average of two estimations of albumen by the gravimetric method was 0.1551 gram albumen in 100 cc. of the urine, hence the difference in results obtained by the two methods is 0.0054 gram in 100 cc. urine.

ALBUMINOUS URINE V.

(1). 20 cc. filtered urine, 10 cc. water.

(a). 5 cc. of the diluted urine required 36.00 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the diluted urine required 36.15 cc. $\frac{1}{5}$ normal KOH, average 36.1 cc., corresponding to 1.1676 gram nitrogen in 100 cc. of the undiluted urine.

(2). 20 cc. filtered urine, 3 cc. Almén's solution, 7 cc. water, mixed and filtered.

(a). 5 cc. of the filtrate required 38.2 cc. $\frac{1}{5}$ normal KOH, corresponding to 0.9912 gram nitrogen in 100 cc. of the undiluted urine. The difference in the quantities of nitrogen found before and after the removal of the albumen is 0.1764 gram, corresponding to 1.1236 gram albumen in 100 cc. of the undiluted urine.

The Gravimetric Method.

The average of two estimations of albumen by the gravimetric method was 1.1292 gram albumen in 100 cc. of the urine; the difference, therefore, in the results obtained by the two methods is 0.0056 gram albumen in 100 cc. urine.

ALBUMINOUS URINE VI.

(1). 20 cc. filtered urine, 10 cc. water.

(a). 5 cc. of the diluted urine required 40.85 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the diluted urine required 40.75 cc. $\frac{1}{5}$ normal KOH, average 40.8 cc., corresponding to 0.7728 gram nitrogen in 100 cc. of the undiluted urine.

(2). 20 cc. filtered urine, 4 cc. Almén's solution, 6 cc. water, mixed and filtered.

(a). 5 cc. of the filtrate required 42.9 cc. $\frac{1}{5}$ normal KOH.

(b). 5 cc. of the filtrate required 42.9 cc. $\frac{1}{5}$ normal KOH, corresponding to 0.5964 gram nitrogen in 100 cc. of the undiluted urine; the difference, therefore, in the quantities of nitrogen found before and after the removal of the albumen is 0.1764 gram, corresponding to 1.1236 gram albumen in 100 cc. of the undiluted urine.

The Gravimetric Method.

The average of two estimations of albumen by the gravimetric method was 1.1279 gram albumen in 100 cc. of the urine; hence the difference in the result obtained by the two methods is 0.0043 gram albumen in 100 cc. of the urine.

ALBUMINOUS URINE VII.

(1). 20 cc. filtered urine, 10 cc. water.

(a). 5 cc. of the diluted urine required 40.4 cc. $\frac{1}{5}$ normal KOH, corresponding to 0.8064 gram nitrogen in 100 cc. of the undiluted urine.

(2). 20 cc. filtered urine, 5 cc. Almén's solution, 5 cc. water, mixed and filtered.

(a). 5 cc. of the filtrate required 41.5 cc. $\frac{1}{5}$ normal KOH, corresponding to 0.714 gram nitrogen in 100 cc. of the undiluted urine.

The difference in the quantities of nitrogen found before and after removal of the albumen is 0.0924 gram, corresponding to 0.5885 gram albumen in 100 cc. of the undiluted urine.

The Gravimetric Method.

The average of two estimations of albumen by the gravimetric method was 0.5953 gram albumen in 100 cc. of the urine. The difference in the results obtained by the two methods is 0.0068 gram albumen in 100 cc. of the urine.

SUMMARY OF RESULTS.

Albuminous Urine.	Per Cent. of Albumen by New Method.	Per Cent. of Albumen by Gravimetric Method.	Difference in Results.
I,	0.4042	0.4399	0.0357
II,	0.0499	0.0506	0.0006
III,	0.8497	0.8557	0.006
IV,	0.1605	0.1551	0.0054
V,	1.1236	1.1292	0.0056
VI,	1.1236	1.1279	0.0043
VII,	0.5885	0.5953	0.0068

By the results of estimations of albumen made by the two methods the average error is 0.0092 per cent., the maximum being 0.0357 per cent., the minimum 0.0006 per cent.

The average error in 35 estimations of albumen made by Dillner,¹ employing the method of Esbach and the gravimetric method, is 0.054 per cent., the quantity of albumen in the urine being from 0.05 to 2.13 per cent.

In 73 per cent. of a great number of estimations of albumen in urine made by O. Hammarsten,² employing Brandberg's method and the gravimetric method, the average error is nearly 0.05 per cent.; however, in many cases the error reached 0.1 per cent.

In estimating albumen in urine by the new method a great excess of tannic acid should not be employed in separating the albumen, as it is oxidised very slowly by sulphuric acid. For ordinary quantities of albumen in urine equal volumes of Almén's solution and urine are sufficient, for small quantities one volume of Almén's solution and two volumes of urine, and in case the albumen is two per cent. the urine should be diluted with water from one to two volumes before making the estimations.

To separate the albumen, 10 cc. of the filtered urine is introduced with 10 cc. Almén's solution into a 50 cc. flask, and after mixing well the fluid is filtered through a dry filter paper into a dry

¹ Esbachs Albuminometer. Upsala Läkareför. Förhand. 21, 1886.

² Upsala Läkareförenings Förhandlingar 18, 130.

beaker. 5 cc. of the filtrate is subjected to the action of 10 cc. concentrated sulphuric acid, as in the original method of Kjeldahl. Whether the dilution of the urine is 1 to 2 or, 1 to 3, the albuminous urine is diluted to the same degree and 5 cc. is employed in Kjeldahl's method. To absorb the ammonia, 10 cc. normal sulphuric acid is employed. In calculating the quantity of albumen in urine from the results of the estimations, instead of subtracting the weight of nitrogen of 100 cc. of the urine proper from the weight of the total quantity of nitrogen in 100 cc. containing albumen, and multiplying the difference by 6.37 for the quantity of albumen, the process may be shortened in the following way: Subtract the number of cc. $\frac{1}{5}$ normal KOH employed in the two titrations, and multiply the difference by 0.0028, and the product of which by 40. The final product is the quantity of nitrogen in 100 cc. of the undiluted urine, which multiplied by 6.37 gives the per cent. of albumen. If the urine is diluted from 1 to 3 volumes in both cases, the weight of nitrogen is multiplied by 60, to obtain the quantity of nitrogen in 100 cc. of the undiluted urine.

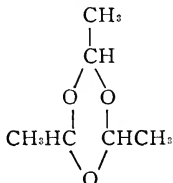
Serum-albumen and serum-globulin, the bodies estimated by the gravimetric method, are not exactly of the same chemical constitution, and hence the employment of the factor 6.37 would not lead to correct results in all cases. The per cent. of nitrogen in serum-globulin, according to Hammarsten, is 15.85, while the per cent. of nitrogen in serum-albumen is 15.7. The factor with which to multiply the weight of nitrogen to obtain the weight of serum-globulin is 6.31 instead of 6.37. As a rule, however, serum-globulin accompanies serum-albumen in the urine in small quantities, so that the number 6.37 may be employed with comparative safety. On the other hand, for exact pathological investigations, the weight of nitrogen of albuminous bodies excreted by the kidneys affords a more certain datum than the quantity of albumen. This is apparent when the fact is taken into consideration that the per cent. of albumen in the urine, as determined by any of the methods now employed, does not represent a definite weight of nitrogen. The new method has the additional advantage of determining the total quantity of nitrogen of the normal nitrogenous constituents of the urine, which, taken into account with the weight of nitrogen of albuminous bodies, is doubtless of importance to the pathologist.

PARAPROPIONIC AND METAPROPIONIC ALDEHYDES.

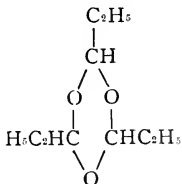
BY W. R. ORNDORFF.

(Preliminary Communication.)

When ordinary aldehyde is treated with hydrochloric acid gas at temperatures below 0° , it is converted into the solid metaldehyde and the liquid paraldehyde. This easy transformation into polymeric bodies seems to be due to the presence in the aldehyde of the carbonyl group, $(-\overset{|}{\text{C}}=\text{O})$. The ready decomposition of the polymerides into the simple bodies when treated with various reagents, and the molecular weight, suggest that the oxygen here plays the part of connecting atoms in the molecule. Thus, when ordinary aldehyde is converted into metaldehyde or paraldehyde, the molecular weight is tripled, and the constitution of paraldehyde and metaldehyde is perhaps represented as follows :



This formula is in accord with all the facts known in regard to metaldehyde and paraldehyde, and has received experimental proof at the hands of Brühl.¹ The next higher homologue of metaldehyde and paraldehyde would have the formula



and would be likely to result from the polymerisation of propionic aldehyde, $\text{C}_2\text{H}_5\text{.COH}$. This substance would probably be more

¹Ann. Chem. (Liebig) **203**, 44.

stable than paraldehyde or metaldehyde, and would perhaps yield substitution products. With this object in view, the attempt was made to prepare the parapropionic aldehyde and metapropionic aldehyde and derivatives.

Parapropionic Aldehyde.

Ordinary propionic aldehyde, boiling at 49° , was cooled in a freezing mixture of ice and salt, and then a few bubbles of hydrochloric acid gas were passed through it. The propionic aldehyde is thus converted very readily into parapropionic aldehyde, and, at the same time, a small quantity of metapropionic aldehyde is also formed. After allowing to stand in the freezing mixture for two or three hours, the metapropionic aldehyde is filtered off, and the parapropionic aldehyde subjected to fractional distillation. A small quantity of liquid distils over below 100° . This was found to consist of propionic aldehyde and a small quantity of parapropionic aldehyde. The larger quantity of the liquid distilled between $160-170^{\circ}$, and, on subjecting this fraction to further distillation, the greater part of it was found to distil at $169^{\circ}-171^{\circ}$, with decomposition into propionic aldehyde. Under a pressure of 50 mm. it was found that it boiled at $85^{\circ}-86^{\circ}$. Thus prepared, parapropionic aldehyde is a colorless liquid, lighter than water, having the odor of ordinary paraldehyde. It solidifies readily, if cooled down to -20° C., to a mass of crystals, resembling in every respect those formed when paraldehyde is cooled down below 0° . It is decomposed by hydrochloric and sulphuric acid, when heated with these acids, ordinary propionic aldehyde being formed, together with a small amount of tarry product.

It is not very soluble in water, and can be separated from ordinary propionic aldehyde by shaking up with water, when the propionic aldehyde dissolves.

Metapropionic Aldehyde.

Ordinary propionic aldehyde was cooled down to -20° and hydrochloric acid gas passed through it. After standing a few hours, the metaldehyde, which had separated out in colorless crystals, was filtered off, and the parapropionic aldehyde formed at the same time was decomposed by heating to the boiling point with dilute sulphuric acid, and passing the vapors through a short Hempel tube to retain the unchanged parapropionic aldehyde.

The propionic aldehyde thus regained was again subjected to the same process, and in this way ten or twelve grams of metapropionic aldehyde were made. This substance is a light crystalline solid resembling ordinary metaldehyde very closely. It is soluble in ether, chloroform and benzene, slightly soluble in alcohol and glacial acetic acid, and insoluble in water. When heated to 165° in an open tube placed in a paraffin-bath, it begins to sublime slowly, melts at 180° , but solidifies again on cooling. Above its melting point it sublimes more rapidly, collecting in the colder portion of the tube. Prof. J. F. Kemp, of the Geological Department, has kindly furnished the following particulars regarding the crystals: "The sublimed crystals are fibrous, acicular. No crystal faces show; merely rounded needles. The longer needles are aggregates of smaller ones, and are fibrous and frayed out. The needles extinguish between crossed nicols along their greatest length, and this corresponds to an axis of elasticity. At other positions they polarise brightly and are distinctly crystalline, though exhibiting no well defined faces. They are not isometric, but more probably hexagonal or tetragonal."

Heated with sulphuric acid, they are readily converted into ordinary propionic aldehyde.

It was found impossible to make any derivatives directly either of parapropionic aldehyde or of metapropionic aldehyde. In every case the products isolated were the same as resulted from treating the propionic aldehyde itself with the various reagents. Further work on these substances was rendered impossible owing to lack of material, but it is proposed to continue the work, and, if possible, to determine the molecular weight of metapropionic aldehyde by Raoult's cryoscopic method. Further, substituted metaldehydes and paraldehydes will probably be made by starting with substituted aldehydes, and the relation existing between metaldehydes and paraldehydes in general will be investigated. It seems highly probable that if the polymerisation of the aldehydes is due to the presence in them of the carbonyl group,

$\begin{array}{c} | \\ (-\text{C}=\text{O}) \end{array}$, polymeric ketones and polymeric acid chlorides can also be formed. For valuable assistance in the experimental part of this work I take pleasure in thanking one of my students, Mr. P. A. Mackay.

Contribution from the Laboratory of General Chemistry, University of Michigan.

THE ACTION OF SODIUM ON ACETONE.

BY PAUL C. FREER.

In a recent article,¹ Beckmann describes a number of reactions between ketones and aldehydes, on the one hand, and metallic sodium on the other; among others, the action of sodium on acetophenone, by which a body $(C_6H_5)_2C \begin{smallmatrix} ONa \\ Na \end{smallmatrix}$ was produced.

This body was extremely unstable, benzhydrele being formed therefrom by addition of water. In the case of Beckmann's reaction there could, of course, be no doubt that one sodium atom was connected to the carbon by means of oxygen. Some time before the paper above referred to appeared, I had occasion to try the action of sodium on acetone, and, as Beckmann does not seem to have followed out this reaction, merely referring to Fittig's preparation of pinacone by the action of sodium on acetone,² I have resumed my investigation of the subject. If acetone be treated with metallic sodium, a reaction takes place which much resembles that of sodium upon ethyl or methyl alcohol. Fittig states that according to Löwig and Weidmann³ no permanent gas is evolved. Apparently Fittig did not, however, attempt to isolate the body formed and study its properties, contenting himself with the preparation of pinacone. Acetone, if pure, yields a white flaky solid on addition of sodium, the whole becoming quite warm, the acetone boiling and some gas being evolved, which is combustible and apparently hydrogen. The greater part of the hydrogen, however, is not given off as such, apparently being used in the reduction of acetone to isopropyl alcohol. This point will be further investigated. After the reaction has continued for some time, a thick, cream-colored paste results, which is the desired sodium acetate. This body, however, is extremely unstable, changing rapidly in the air, becoming dark red, giving, apparently, pinacone and some high-boiling oily products. Much better results are obtained if the metallic sodium is finely powdered and covered with a large amount of anhydrous ether, the acetone mixed with four or five times its own volume of the

¹ Ber. d. chem. Gesell. **22**, 912.

² Ann. Chem. (Liebig) **110**, 25; **114**, 54.

³ J. prakt. Chem. **21**, 54.

same medium, and then slowly added to the sodium by means of a drop-funnel, the whole operation being conducted in a stream of dry and pure hydrogen. By this means the reaction is rendered less violent, and the sodium derivative separates as a white substance. Less reduction of the acetone also takes place, for, when the operation is conducted in a flask with delivery-tube, no hydrogen being added from without, a considerable quantity of a gas, insoluble in water and alcohol, and combustible, apparently hydrogen, is obtained. When all of the metallic sodium has disappeared, the resulting insoluble body is quickly filtered, and, after being spread on a porous plate, is freed from ether over solid paraffin in a vacuum. This part of the operation must be conducted with the greatest celerity, as the body is instantly turned pink by exposure to the atmosphere. Even when the whole takes but one or two minutes, the sodium determinations always show an excess of sodium over that calculated for $\text{CH}_3 - \text{CONa} - \text{CH}_3$.

I. .4760 gram substance gave .4434 gram Na_2SO_4 .

II. .5525 gram substance gave .5547 gram Na_2SO_4 .

	Calculated.	I. Found.	II.
Na	28.75 per cent.	30.17	32.63

The results of these analyses prove, at least, that there is one atom of sodium to one of acetone, thus bringing the body in line with acetoacetic ether, for, presumably, the reaction which takes place is the replacement of one atom of hydrogen by one of sodium. The sodium compound on being added to dilute hydrochloric acid regenerates acetone, which was detected in the liquid by means of the iodoform test and by the formation of the soluble compound of acetone with the precipitated oxide of mercury. If the sodium compound be exposed to the air for some time and then added to dilute hydrochloric acid, an oil is also formed which probably corresponds to some of the bodies obtained by Fittig.¹

In order further to prove the composition of the body, an attempt was made to convert it into acetoacetic ether by the addition of chlorocarbonic ether. If this latter substance be added to the sodium derivative suspended in ether, a reaction at once takes place, sodium chloride is formed, and, on the addition of water, drying of the ethereal solution, and evaporation of the ether,

¹Ann. Chem. (Liebig) 110, 25.

an oil remains which on fractional distillation seems to be composed of several bodies. The greater portion, however, boiling between 185° – 200° , was not identical with acetoacetic ether. What these bodies are I am not at present able to state, but I should like to reserve for myself the future investigation of this interesting subject. I should like to return thanks to Mr. G. O. Higley, who has assisted me in the work.

April, 1890.

REVIEWS AND REPORTS.

RECENT SYNTHETICAL EXPERIMENTS IN THE SUGAR SERIES.

Professor Emil Fischer's researches on the sugars of the glucose group have been remarkably successful, and recently he has effected the synthesis of both dextrose and levulose. A year ago, in this journal,¹ the experiments were described by means of which he had succeeded in preparing a new synthetical sugar, which he called acrose, and which was found to be an isomer of dextrose and levulose. Acrose possesses all the general properties of dextrose and levulose, and only differs from these natural sugars in being optically inactive. Fischer has now succeeded in determining the constitution of acrose, and in his recent papers² he has shown that it is the inactive modification of levulose. It bears the same relation to ordinary levulose that racemic acid bears to ordinary tartaric acid; and just as racemic acid can be split into dextro- and levo-tartaric acids, so from acrose ordinary levulose and a new levulose having an equal but opposite rotatory power, can be obtained.

The obstacles that are encountered in this kind of work are very great, and one can gain some idea of the difficulty of determining the constitution of a sugar by remembering that, according to the Le Bel-Van't Hoff hypothesis,³ a compound with four asymmetric carbon atoms like dextrose can exist in sixteen stereometric forms. Nevertheless Fischer has not only determined the constitution of acrose and effected the synthesis of levulose, but he has also discovered the inactive and the levo-modifications of mannite and of the new sugar mannose. He has shown that mannose and dextrose have the same constitution and that one may be converted into the other. He has further prepared all these substances synthetically,

¹ This Journal **11**, 277.

² Ber. d. chem. Ges. **23**, 372, 376.

³ Van't Hoff. *Dix années dans l'histoire d'une théorie*, p. 54.

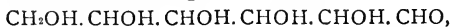
and, what is also of very great importance, he has developed and perfected the methods of transforming the sugars and their derivatives into one another to such an extent that the synthesis of the remaining members of the glucose group will probably be effected in the near future. In fact, so great are the additions to our knowledge resulting from these researches that Fischer's work may well be said to mark the beginning of a new epoch in the history of the carbohydrates.

Mannose.

This new sugar was discovered by Fischer¹ in studying the oxidation products of the poly-acid alcohols with the aid of phenylhydrazine. It is obtained, together with levulose, by the oxidation of mannite with nitric acid, and it can readily be distinguished from the other sugars on account of the insolubility of its hydrazone. Mannose has the composition represented by the formula $C_6H_{12}O_6$, and is therefore isomeric with dextrose and levulose, and, like these, it reduces Fehling's solution, and undergoes fermentation when mixed with yeast. It is optically active, and turns the plane of polarised light to the right, but not so strongly as dextrose. Its specific rotatory power is $+12.96$, that of dextrose being $+58.7$. Reduction with sodium amalgam converts it into mannite. Mannose has not yet been obtained in crystalline condition. The white solid sugar deliquesces rapidly in moist air, and is extremely easily soluble in water. It dissolves with difficulty in absolute alcohol, and is insoluble in absolute ether. Like dextrose and levulose, mannose can be converted into furfural and levulinic acid. Treatment with bromine water converts it into mannonic acid, an isomer of gluconic acid.

But the distinguishing characteristic of mannose is its behavior with phenylhydrazine. The cold aqueous solution of the sugar, when treated with phenylhydrazine, gives at once a crystalline precipitate of mannose phenylhydrazone, whereas the hydrazones of dextrose and levulose and the other sugars are readily soluble in water. When heated with more phenylhydrazine, the mannose hydrazone is converted into an osazone, which is identical in all its properties with phenylglucosazone, the compound that is obtained from dextrose and levulose under similar circumstances. As glucosazone can be converted into levulose, it is therefore possible by this means to transform mannose into levulose.

*Constitution of Mannose.*²—As mannose differs in properties from both dextrose and levulose, it was at first supposed that its constitution was different from that of either of these sugars. Thus the formula of dextrose being



¹ Ber. d. chem. Ges. **21**, 1805; **22**, 365.

² Ibid. **22**, 365.

and that of levulose

$\text{CH}_2\text{OH} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{CO} \cdot \text{CH}_2\text{OH}$,
 the formula $\text{CH}_2\text{OH} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{CO} \cdot \text{CHOH} \cdot \text{CH}_2\text{OH}$
 suggested itself for mannose. In order to obtain experimental evidence either for or against this formula, mannose was treated with hydrocyanic acid, according to Kiliani's¹ method of determining the constitution of sugars. Direct addition took place, and from the resulting compound mannose-carbonic acid was obtained. This acid, upon reduction with hydriodic acid, was converted into normal heptonic acid. This result indicates that the constitution of mannose cannot be represented by the formula given above, because a sugar whose constitution is represented by that formula would by this process have been converted into an isoheptonic acid. But the fact that normal heptonic acid was obtained indicates that mannose contains an aldehyde group, and that its constitution must be expressed by the same formula as that which represents the constitution of dextrose. Mannose and dextrose are, therefore, physical isomers. To explain this isomerism recourse must be had to the Le Bel-Van't Hoff hypothesis, according to which it is possible to foresee the existence of eight optically active and eight inactive compounds of the formula of dextrose. Both compounds are dextro-rotatory, but as one of them turns the plane of polarised light to a much greater extent than the other, Fischer at first supposed that dextrose and mannose were optical isomers, that they were the dextro and levo-modifications of the same structural system, and that the rule which usually holds in such cases, namely, that the one isomer turns as far to the left as the other to the right, was modified in this case in some unknown manner by the remaining asymmetric carbon atoms. This supposition was not confirmed by subsequent experiments, for, as will be shown below, another mannose similar in all its properties to the one here described, but possessing an equal but opposite rotatory power, was obtained from arabinose carbonic acid.

Reduction of the Acids of the Sugars.²

Before proceeding to describe how the optical isomer of mannose was obtained, it is necessary to call attention to a reaction which is of some importance, and which is a general one for the acids of the sugar series. Ordinarily the carboxyl group of organic acids cannot be reduced to the aldehyde group by means of nascent hydrogen. This reduction, however, takes place readily, as has been discovered by Fischer, in the case of the sugar acids that yield lactones. If gluconic acid lactone, for example, be treated with sodium amalgam, and the solution be acidified from time to time, it soon acquires the power of reducing Fehling's solution, and by continued action a solution of sugar is

¹ Ber. d. chem. Ges. 21, 916.

² Ibid. 22, 2204.

obtained. The solution contains dextrose, and when it is treated with phenylhydrazine it gives glucosazone. In the same way mannonic acid, obtained by the oxidation of mannose with bromine water, was reduced with sodium amalgam and mannose again obtained. Other sugar acids behaved in the same way—in short, the method appears to be a general one, and one of very great importance in connection with the synthesis of the sugars. It is possible by means of this method, together with Kiliani's reaction, to build up a sugar from one containing a smaller number of carbon atoms. For, by treating a sugar with hydrocyanic acid, an addition product is obtained from which an acid containing one carbon atom more than the original sugar can be prepared. This acid can then be reduced with sodium amalgam, and thus converted into the corresponding sugar. The process of lengthening the chain of carbon atoms can then be repeated. Thus far only acids that form lactones have been reduced with sodium amalgam, and it appears that this property is in some way connected with the power of forming lactones.

Synthesis of Mannose and Levulose.¹

When mannose is oxidised with bromine water it is converted into mannonic acid. A thorough examination of the properties of mannonic acid showed that it has almost identically the same properties as arabinose-carbonic acid. The latter compound was discovered by Kiliani,² and is obtained from the addition product which is formed by the union of hydrocyanic acid and arabinose. The lactones of these acids are so similar in properties that they would be regarded as identical were it not for the fact that they rotate the plane of polarised light in opposite directions. As their rotatory power is very nearly equal but in opposite directions, it seemed very probable that they were optical isomers. This supposition proved to be true, for, on mixing solutions of equal weights of the two lactones, an optically inactive compound of the same composition was obtained. This inactive lactone can be transformed into inactive salts and other derivatives, and it is only possible by certain special methods, to be described below, to again resolve it into its optically active constituents. The three lactones can by reduction be converted into sugars, and these in turn into three hexacid alcohols, and the corresponding members of these three series of reduction products bear the same relation to each other as do the original lactones. Thus, from the lactone of mannonic acid, mannose and ordinary mannite are obtained, while from the lactone of arabinose-carbonic acid, a levo-mannose and a levo-mannite are obtained; and finally, reduction of the inactive lactone gives two corresponding inactive derivatives. The relation of these compounds is shown by the following table:

¹ Ber. d. chem. Ges. **23**, 370.

² Ibid. **19**, 3034.

<i>d</i> -SERIES.	<i>i</i> -SERIES.	<i>l</i> -SERIES.
<i>d</i> -Mannonic acid lactone (dextro-rotatory).	<i>i</i> -Mannonic acid lactone.	<i>l</i> -Arabinose-carbonic acid lactone (levo-rotatory).
<i>d</i> -Mannonic acid.	<i>i</i> -Mannonic acid.	<i>l</i> -Arabinose-carbonic acid.
<i>d</i> -Mannose (ordinary) (dextro-rotatory).	<i>i</i> -Mannose.	<i>l</i> -Mannose (levo-rotatory).
<i>d</i> -Mannite (dextro-rotatory).	<i>i</i> -Mannite (α -acrite).	<i>l</i> -Mannite (levo-rotatory).
<i>d</i> -Mannose phenylhydrazone (levo-rotatory).	<i>i</i> -Mannose phenylhydrazone.	<i>l</i> -Mannose hydrazone (dextro-rotatory).
<i>d</i> -Phenylglucosazone (levo-rotatory).	<i>i</i> -Phenylglucosazone (α -acrosazone).	<i>l</i> -Phenylglucosazone (dextro-rotatory).

To avoid confusion, the compounds of the three series are designated by prefixing the letters *d*, *i* and *l* to their names according to the rotatory power of the sugar of the series. The letter *d* or *l* before the name of a compound does not necessarily imply that the compound is either dextro- or levo-rotatory, but merely that it is a derivative of a dextro- or levo-rotatory sugar. Thus the two phenylhydrazine derivatives of *d*-mannose are levo-rotatory.

In a recent paper¹ the preparation and properties of the new sugars *l*-mannose and *i*-mannose and their derivatives are described. Both of them, like *d*-mannose, are stereometric isomers of dextrose. *l*-Mannose can only be fermented with great difficulty, and, like *d*-mannose, it is characterised by the insolubility of its hydrazone. *l*-Phenylglucosazone is the optical isomer of ordinary or *d*-phenylglucosazone, and *l*-mannite of ordinary *d*-mannite.

That *i*-mannonic acid is really the optically inactive modification of *d*- and *l*-mannonic acid was shown by splitting it up into its two active components. Two methods were used for this purpose; the first one consisted in subjecting it to fermentation with penicillium glaucum. The *d*-mannonic acid was consumed by the ferment, while the *l*-acid remained behind and was isolated. The second method depended upon the unequal solubility of the strychnine salts of the two acids in absolute alcohol; the salt of the *d*-mannonic acid being much more soluble than the *l* variety, can be readily separated from the latter. A separation of the optically active constituents of *i*-mannose was brought about by fermentation with yeast. When yeast acts upon *i*-mannose, the *d*-mannose is rapidly consumed and the *l*-mannose remains behind.

Perhaps the most important and interesting discovery² made

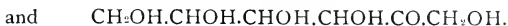
¹ Ber. d. chem. Ges. 23, 373.

² Ibid. 23, 383.

in the course of this admirable investigation was the observation that *i*-mannite and α -acrite are identical substances. α -Acrite, it will be remembered, is the hexacid alcohol obtained by the reduction of acrose, the new synthetical sugar which had been built up from glycerin, acrolein bromide and from formic aldehyde. α -Acrite has identically the same properties that *i*-mannite has, and, like the latter compound, it can be converted into *i*-mannose. α -Acrosazone also is identical with *i*-phenylglucosazone. As, therefore, acrose and *i*-mannose give the same osazone with phenylhydrazine, it follows that the constitution of acrose must be represented by one of the two formulas:



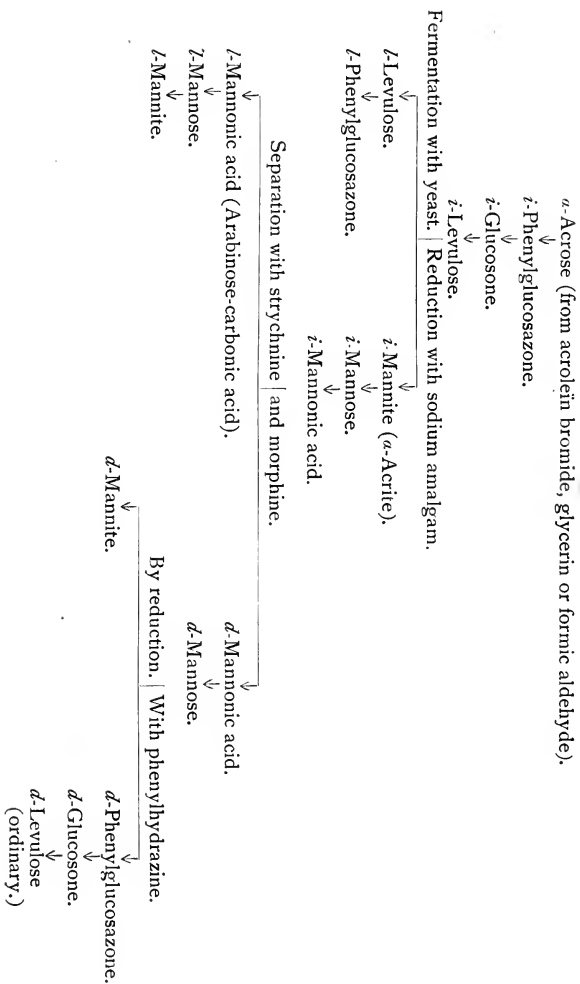
i-Mannose.



i-Levulose.

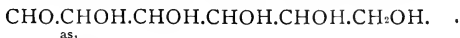
If acrose has the constitution represented by the first one, then it is identical with *i*-mannose, and, like the latter substance, it ought to give a difficultly soluble hydrazone when its solution is treated with phenylhydrazine. Acrose was, therefore, prepared by direct synthesis from acrolein bromide, and its solution was tested with phenylhydrazine. Under no circumstances could the formation of an insoluble hydrazone be observed. This result, therefore, leads to the conclusion that acrose is *i*-levulose, and its constitution must be represented by the second formula. The synthetical sugar obtained from α -acrosazone was also examined in the same way, and, as was to be expected, it also proved to be *i*-levulose.

Further evidence in favor of the view that acrose is *i*-levulose was obtained by observing the changes which it undergoes upon fermentation. When acrose was mixed with yeast, it was found that one of the optical components, *d*-levulose, was consumed much more rapidly than the other, and after the fermentation had continued for some time, the *l*-levulose was recognised and separated from the solution by means of its osazone. So also the α -acrite, like *i*-mannite, was converted into *i*-mannose and *i*-mannonic acid. But the latter compound can be separated into its optically active constituents, and these in turn can be transformed, on the one hand, into *l*-mannose and *l*-mannite, and on the other hand into ordinary mannose and mannite, and into levulose. Thus the complete synthesis of levulose and of the three series of mannite derivatives has been effected. The successive steps in the synthesis are indicated in the following table.



Synthesis of Dextrose.

As has been shown above, *d*-mannose and dextrose have the same constitution and must be regarded as stereometric isomers. Both sugars give the same osazone when treated with phenylhydrazine. It follows, therefore, that the difference between them is due to the asymmetry of the carbon atom as_1 in the formula:



Fischer also regarded it as highly probable that in mannose the carbon atom as_1 was optically inactive, and that it plays a rôle similar to that of the two carbon atoms in racemic acid. If this supposition is true, then mannonic acid would be related to gluconic acid in the same way that racemic acid is related to one of the active tartaric acids, or this relationship would be analogous to that of racemic acid to mesotartaric acid. In his last paper¹ Fischer shows that the latter is the true relation. Each of these acids can be transformed into the other. When either one is heated with quinoline to a temperature of 140° , a mixture of the two acids is obtained. This transformation is analogous to that which has been observed in the case of racemic and mesotartaric acids. When either one of these is heated with water to a temperature of 170° – 180° , a mixture of both is obtained.

For the purpose of preparing dextrose, mannonic acid was heated with quinoline, and from the mixture of acids thus obtained the gluconic acid was separated by means of its brucine salt. The brucine salt was decomposed, and the gluconic acid was found to be identical in properties with the gluconic acid obtained by the oxidation of dextrose. The acid was thereupon reduced with sodium amalgam, and from the liquid, *anhydrous crystalline dextrose*, identical in all its properties with ordinary dextrose, was obtained.

The synthesis of dextrose, therefore, is achieved, for, as will be seen in the table printed above, *d*-mannonic acid has been prepared from acrose, and acrose has been made from formic aldehyde.

E. H. KEISER.

¹Ber. d. chem. Ges. **23**, 793.

AMERICAN CHEMICAL JOURNAL.

A SYSTEMATIC STUDY OF THE ACTION OF DEFIN- ITELY RELATED CHEMICAL COMPOUNDS UPON ANIMALS.

BY WOLCOTT GIBBS, M. D., *Rumford Professor (Emeritus) in Harvard University*, AND H. A. HARE, M. D., *Demonstrator of Therapeutics and Instructor in Physical Diagnosis in the Medical Department and in Physiology in the Biological Department of the University of Pennsylvania.*

(Continued from p. 152.)

Ortho-toluidine, when injected into the posterior lymph-sac of a frog, so that .017 gram of drug is present for each gram of frog, causes loss of reflexes and respiration, which comes on at once, and the animal lies wherever he is placed. The muscles and nerves respond to stimuli, but their irritability is decreased, and it is noted that reflexes are more depressed in the hind than in the fore feet. After this the reflexes improve and become almost excessive. The heart is at this time very weak, and stops shortly within an hour of the dose, in wide diastole. The reflexes are still present, but lessened for the second time. The muscles and nerves respond feebly for many minutes after death. Doses amounting to 0.001 gram have a similar effect.

If a single drop be applied to the exposed spinal cord of the frog, paraplegia at once comes on, motion being preserved in the fore legs. That the failure of motion and sensation which we have noted is dependent upon some action on the spinal cord is

proved by the fact that the direct application of the drug, in the amount of one pure drop, to the exposed sciatic nerve caused very slight, if any, failure in functional activity, although extra precaution was taken that none of it should be taken by the circulation elsewhere. The loss of reflexes which at first is present we believe to be due to depression of the spinal cord, and the increase in reflex activity which later occurs to be due to some action which our present physiological knowledge does not allow us to explain, or to the disordered circulation by means of which the spinal cord is starved, so that at first its irritability is increased but finally abolished.

When applied directly to the heart of the frog in the amount of one drop, it arrests this viscus in diastole in a few minutes.

Upon the dog our results have been in accord with those in the frog. If ortho-toluidine be injected into the jugular vein, in the amount of 0.12 gram to the kilo, there is some slight change for a few moments in the rhythm of respiration, followed by quietude. Sensation is intact and so is motion. The rectal temperature is depressed 1.5° F., then speedily returns to the normal. One hour after the dose the animal seems perfectly well. No staggering occurs.

If given in so large a dose that 0.208 gram to the kilo is injected in 20 cc. water into the jugular vein, the animal instantly becomes passive and lies absolutely quiet, except that respiration is hurried. The tongue is dark blue, cyanotic and lead-colored. The pupils dilate. When put on the floor the dog cannot walk at first, but in one or two minutes can stagger about the room, the hind legs being most affected. Five minutes after the injection he can walk moderately well, but in 25 minutes after the dose he again becomes weak, staggers badly and leans against the wall for support, and falls when support is lost. The tongue, nose and mouth are now extraordinarily pale or livid. The rectal temperature is noted as having fallen 1.5° F. since the dose, and absolute muscular relaxation comes on. The respirations are slow and shallow, but expiration is forcible and quick. Consciousness is absolutely intact. The animal wags his tail feebly when spoken to. Grunting and groaning now come on with each breath, and the symptoms become more severe. The rectal temperature is now found to have fallen 1° F. more. Later forcible vomiting comes on, consisting of water and the contents of the stomach. The eyes

become glazed and death seems close at hand. The temperature is now 99° F., having been normally 104° F. The respiration ceases suddenly, and at the same moment a large amount of bloody liquid, resembling methæmoglobin in color, is ejected from the stomach. The heart ceases beating three minutes later. These results correspond to those seen in the frog in respect to the return of motion after its primary loss, and the fact that respiration ceased before the heart. The loss of reflex motion and the general muscular relaxation are also identical. The peculiar bloody watery liquid ejected was probably due to a leakage of broken down blood from the mucous membrane of the stomach, owing to the great blood-changes produced by the drug, as no ruptured blood-vessels could be found.

It is worthy of remark that ortho-toluidine lowers the bodily temperature in large amounts, as do all the other members of the aniline group.

When injected in the dose of 0.05 gram to the kilo, into the jugular vein of a dog which is attached to a manometer, ortho-toluidine, in the course of about one minute and a half, causes a slight fall of pressure, accompanied by no marked change in pulse-rate, and the pressure speedily returns to the normal or even a little above it. Fifteen minutes later 0.1 gram to the kilo in 20 cc. water was injected in 20 seconds, the result being that the pressure fell very markedly, and the pulse-rate was also decreased nearly one-half. The latter, however, speedily returned to the normal, as did also the arterial pressure some seconds later. One decigram more to the kilo at this time, 16 minutes after the first dose, caused death by respiratory failure, the heart continuing to beat till some minutes later. The slowing of the pulse-rate is due to direct cardiac depression, and not vagal irritation, as is proved by the fact that severing these nerves does not cause the proper increase in rate. In other animals death took place two minutes after the injection of 0.3 gram to the kilo, preceded by a gradual fall of pulse rate and pressure, which vagal section did not relieve. As these results were reached in curarised and non-curarised animals, it would seem that they must be correct.

Meta-toluidine.

When meta-toluidine is given to a full-grown dog by the jugular vein in the dose of 0.125 gram to the kilo, death at once occurs

from cardiac and respiratory failure, both functions ceasing at once. If any difference as to time occurs, respiration ceases first. When the dose by the jugular vein is 0.010 gram to the kilo, the changes produced in pulse rate, force and arterial pressure are almost nil.

If the dose be as large as 0.06 gram to the kilo, there is very marked fall of blood-pressure, followed, after a period of 30 seconds to a minute, by a rise which soon returns the arterial pressure to the normal. There is always a considerable fall of temperature in small doses. Meta-toluidine given to a dog by the jugular vein in the dose of 0.1 gram to the kilo, when free to run about, and to which no ether has been given, produces at first the greatest weakness and relaxation, so that the animal seems about to die. This rapidly passes off, so that he can soon walk in a slouchy way around the rooms and lies in a corner whenever he is allowed to do so. In the dose of 0.05 gram to the kilo virtually no change occurs so far as symptoms are concerned, save a little drowsiness. The blood always contains methæmoglobin, and is much darkened and grumous. In the frog there ensues rapidly, after a dose of 0.0015 gram to the gram into the post. lymph-sac, relaxation with arrest of all respiration, only the throat moving a little. The limbs become cyanotic, and the batrachian will soon lie on his back when so placed. Marked inco-ordination of leg movements occurs, but there seems to be no loss of motor power. Sensation is completely lost to all forms of irritation, save severe burning, and this soon passes off. Voluntary movement is preserved partially. The motor nerves are depressed, but react to stimuli. If the artery going to one limb be ligated and the poison given above, it will be found that both legs fail equally, proving that the action must be on the spinal cord, or, at any rate, not on the motor nerves. The meta-toluidine employed was prepared in the laboratory of Prof. Ira Remsen, to whom our grateful acknowledgments are due.

*Para-toluidine.*¹

If this compound be given to a dog by the stomach in the dose of 0.13 gram to the kilo, all the symptoms of aniline poisoning gradually appear. If the same dose be injected *exceedingly slowly*

¹ It is proper to state that as para-toluidine is very insoluble, Dr. Marshall kindly prepared para-toluidine hydrochloride, a substance which is comparatively easily dissolved and administered.

into the jugular vein of an animal, struggles which are mild, but lacking in force, come on before the entire quantity has passed out of the syringe. When laid upon the floor and left free to run about, inability to stand, particularly in the hind legs, comes on, but eventually, in the course of about two minutes, sufficient power is gained to enable the animal to walk about in a staggering manner. The respirations are more rapid than normal, and the expiratory portion of the respiratory cycle is forcibly performed, so as to be almost sneezing in character. The pupils are much dilated. Half an hour after the dose the animal seems almost well, except for the expiratory movements which continue, and which finally accompany, an hour later, great lassitude and desire to remain quiet. From now on the dog becomes slowly but progressively worse, and is evidently more ill than before, dying at the expiration of two hours from the injection of the drug.

No change takes place in the bodily temperature during the first three hours, but as the symptoms of paralysis deepen, the temperature finally reaches a point several degrees below normal. Unconsciousness comes on and death takes place, the animal being utterly unconscious to all its surroundings. The blood is found to be dark-colored, abnormally fluid, and methæmoglobin is present in large amount. If the dose be as much as 0.3 gram to the kilo, the animal passes much more rapidly through the same train of symptoms as those just given, but they are also much more emphasised.

The primary struggles which come on during the injection of the drug are due to cardiac depression and the resulting nervous disturbance, as they do not occur if the dose be given with great slowness, nor when the drug is given by the stomach; and we are confirmed in this belief by our manometrical tracings, which show that such a cardiac influence is present. The other symptoms are solely due to the disorganised blood.

When from 0.02 to 0.05 gram of para-toluidine hydrochloride is injected into the body of a frog weighing 36 grams, the reflexes are rapidly lost, and the batrachian will lie for some minutes on his back when so placed by the experimenter. The fore feet and hind legs rapidly become blue and cyanosed, and, while the reflexes are still present, they are exceedingly feeble and carried out in an inco-ordinated and jerky manner.

As these changes occur in the bloodless as well as in the ordi-

nary frog, they are at least in part due to an action on the spinal cord. That the nerves and muscles are eventually depressed we have proved again and again, but we believe this depression to be due to the altered blood, as we did not find it in the exsanguined animal.

If the heart be exposed it is seen to be beating regularly, but the blood is darker than normal. Very frequently, nearly an hour after the dose, the reflexes return to a point equal to their normal condition or above it, but are always inco-ordinated. Finally the animal lies perfectly quiet, the heart beats much more slowly, and at this time the very curious observation is made that the auricle beats twice as frequently as does the ventricle; the latter also stops before the former. The same result is reached if a single scale of the compound be placed directly on the heart-muscle of a frog whose anterior chest-wall is cut away to expose the viscus. The result under these circumstances is indeed more marked. Preceding the double beating of the auricle there is a period during which that portion of the heart seems over-distended with blood. The heart is always slowed, before these curious changes take place, by nearly one-half.

Para-toluidine, when given by the jugular vein to a dog in the proportion of 0.10 gram to the kilo, causes death of respiratory failure in 30 seconds, the heart continuing to beat for some minutes later. *Pari passu* with the arrest of respiration there is a very positive fall of pressure, eventually reaching the abscissa line. The heart-beats are not weakened till death is very near at hand, and show evidence of asphyxia, while the slowing was proved to be independent of vagal stimulation by its occurrence on section of these nerves. That the vaso-motor system is also depressed is certain, for though, as we have just related, the heart is moderately strong, a fall in blood-pressure occurs notwithstanding the asphyxia which is brought on by the arrest of respiration. Exactly the same signs follow the injection of 0.08 gram to the kilo.

When injected into the jugular vein in the proportion of 0.031 gram to the kilo, no change in arterial pressure occurs, but in the course of a few minutes the pulse-rate becomes much increased. Stimulation of the vagi at this time causes the normal amount of slowing of the heart, showing that the increased rate cannot be due to vagal depression.

SUMMARY.

Ortho-toluidine, both in the frog and dog, causes great changes in the blood and has comparatively little effect upon the heart, unless it comes directly in contact with this viscus in large amount or concentrated form. In both animals it produces a stage of decreased reflex activity and power, followed by a decrease in both these functions, which deepens into paralysis, coma and death.

The main dominant action of the compound is the breaking down of the blood, but that the entire train of symptoms do not depend on this change is shown by the fact that the drug depresses the spinal cord in the bloodless frog. In the warm-blooded animal it causes a marked fall of temperature equal to 4 or 5 degrees. Death is produced by failure of respiration. The heart eventually stops in diastole.

On the circulatory system this substance slows the pulse by depression of the heart-muscle, and does not stimulate the pneumogastric nerves. It also depresses the vaso-motor system.

On the dog and frog meta-toluidine changes the blood into methæmoglobin and produces a loss of reflex activity, dependent upon depression of the spinal cord. It lowers bodily temperature very remarkably, and exercises very little effect on the circulation unless given in exceedingly large doses. It kills chiefly by failure of respiration, unless sent *en masse* into the heart, when it kills by cardiac and respiratory failure of a simultaneous action.

In the frog and dog the results reached with para-toluidine are identical with those of the ortho and meta compounds in the primary depression, secondary increase and final loss of reflex activity and power, so that in this respect para-toluidine and ortho-toluidine are very closely allied. The dominant action is also the destruction of the blood corpuscles and the development of methæmoglobin. It also depresses the spinal cord and kills by failure of respiration, the heart beating for some moments afterwards. The most extraordinary fact noted in regard to the compound is the double beat of the auricle to the single beat of the ventricle in the frog's heart. If brought in direct contact with the heart of the frog or mammal in large amount, it arrests this viscus in diastole. Small doses, 0.031 gram to the kilo, increase the pulse-rate, which stimulation of the vagi instantly controls. The fatal dose of ortho-toluidine by the jugular vein is 0.208 gram

to the kilo ; of meta-toluidine, 0.125 gram ; of para-toluidine, 0.10 gram to the kilo. It is worthy of note that the lethal doses of these compounds depend upon the rapidity of injection to a very great extent. The ortho-toluidine and para-toluidine came from the establishment of Kahlbaum in Berlin.

Pyrocatechin.

Pyrocatechin, the ortho member of the group about to be considered, seems, unlike most of the compounds already studied, to be more powerful by far than the meta compound, and even more active than the para compound, hydroquinone. The injection of small quantities of pyrocatechin into the jugular vein, such as 0.0166 gram to the kilo, of the dog, produces at once epileptiform convulsions and all the evidences of poisoning by this class of compounds. The blood rapidly becomes blackish. The periods of spasms are long-continued and exceedingly severe, and death seems to occur from exhaustion and respiratory failure when the dose has been as large as 0.04 gram to the kilo. When the dose is by the stomach, a much larger amount is required. The same train of symptoms ensue under these circumstances as occur when the drug is given by the jugular vein. When given by the jugular vein, in the dose of 0.0166 gram to the kilo of dog's weight, the animal being attached to the manometer, pyrocatechin causes, along with the muscular twitchings and convulsions, a marked slowing of the pulse, the arterial pressure remaining little changed. If the dose be as large as 0.0384 gram to the kilo, the pulse is also slowed, and during the convulsion the arterial pressure is somewhat raised. Finally, however, the pulse remaining at its point of primary change, the arterial pressure sinks lower and lower, and the animal dies of respiratory failure, the respiration ceasing before the heart, which beats for some moments later. If the dose be as large as 0.075 gram to the kilo, the pulse at once becomes slower by many beats, the arterial pressure remaining almost unchanged. That this slowing of the pulse, seen also after smaller doses, is not due to the convulsions, but to vagal stimulation, is proved by the fact that it occurs in the curarised dog, and also by the all-important fact that section of these nerves at once causes as rapid a pulse-rate as in the undrugged animal under such an operation. The pulse-waves during this time are very full and strong, and the heart-beat is forcible.

The results of Brieger's studies, which are entirely confirmed by our own, may be seen in the summing up of the action of these drugs under hydroquinone.

Resorcin.

The employment of resorcin in therapeutics, both for internal and external medication, increases the interest attached to its study very considerably, and we find that other investigators have already made considerable progress in finding out its true physiological action. None of the researches which we have been able to find give, however, the relations of the drug as a meta compound, although physiologists have in two instances studied the ortho and para compounds, pyrocatechin and hydroquinone, at the same time. These investigations we shall refer to later, mentioning them after detailing our results, because the papers were read after our own studies were made, but of course acknowledging their priority.

Resorcin when injected into the jugular vein of a dog attached to a manometer, in the dose of 0.0143 gram to the kilo, produces a slight fall of arterial pressure, and slowing of the pulse to a slight extent. If the dose be as large as 0.1666 gram to the kilo of the animal's weight, this fall of pressure becomes still more marked, as does also the slowing of the pulse. That this fall of the arterial pressure is dependent on an action upon the vaso-motor system seems proved by the fact that the heart-beats give no evidence of cardiac depression, and asphyxia does not produce as great a rise of pressure as it should do. The slow pulse noted may be due to several causes, the convulsions, with the violent breathing and resulting heart-strain, the action of the drug on the heart itself or on the vagus nerve. That the convulsive breathing is partly responsible for this seems proved by the fact that the same degree of slowing does not occur in the curarised animal, although it occurs to a decided extent nevertheless. That the heart is not depressed seems equally clear by reason of the strong pulse beats, and finally the vagus nerve is stimulated, since vagal section at this time allows the heart to double its number of beats, although they do not approach those of the normal dog whose vagi are cut, pointing to stimulation of their peripheral filaments. If the dose of 0.4 gram to the kilo is used there is a great fall of blood pressure, amounting to from 30 to 140 mm. of mercury, accompanied by very marked slowing of the pulse, due to the vagal stimulation.

The convulsions produced are exceedingly severe. When injected in the dose of 0.1 to 0.4 gram to the kilo, into the jugular vein in the dog free to run about, the symptoms consist in violent epileptiform convulsions, in which the animal is thrown about hither and thither and utterly unable to stand. The lethal dose by the jugular vein is about 0.7 to 1 gram to the kilo. Death is due to respiratory failure, probably from the action of the blood. These studies confirm those of Brieger¹ and Beyer.²

In the frog, Brieger noted that the dose of 0.005 gram of resorcin to 55 grams of frog produced convulsions followed by recovery; that 0.01 gram to a larger frog caused similar convulsions and death in six hours; very much smaller doses produced mild convulsions, and still smaller ones no convulsions at all. In the rabbit, Brieger found the dose of 0.33 gram to the kilo, by the mouth, caused convulsions for two hours, but the animal recovered in a day.

In the studies made by Beyer upon the isolated heart of the frog and terrapin, he found that solutions of 1 to 1000 of resorcin have no appreciable influence on the rate of the heart-beat or the work done by that viscus, but that stronger solutions of the strength of 20 to 1000 reduced the rate and force and rapidly caused diastolic arrest. His conclusions are that in small doses it stimulates the heart, and in larger doses stops it in diastole. Beyer also asserts that it slows the pulse by acting on the peripheral vagi, a conclusion confirmed by our own studies. We can also endorse his assertion that small doses stimulate the heart, as we found that in the intact dog the dose of 0.0714 gram to the kilo had this effect.

Hydroquinone.

Like the meta compound, hydroquinone (para) has been used in medicine as an antipyretic, but its value in therapeutics is exceedingly limited. Given to a dog in the dose of 0.033 gram to the kilo by the jugular vein, the animal being free to run about, hydroquinone produces great staggering and convulsions, with a somewhat quickened respiration. After being convulsed for from two to three minutes gradual recovery occurs, the animal being almost as well as before after the lapse of 15 minutes. Later a renewal of the convulsions may take place. Along with the con-

¹Archiv für Physiologie: Du Bois Reymond, 1879. Supplement Band, p. 61.

²American Journal of Medical Sciences, April, 1886.

vulsions there is a marked exophthalmia and running movements, the convulsions being epileptiform. The blood is black and inky looking. When the dog is attached to the manometer and 0.166 gram to the kilo of his weight is injected into his jugular vein, the tracing becomes largely altered by reason of the convulsions which ensue, the pulse-rate is considerably increased, but the arterial pressure progressively falls until the drop equals about 70 mm. of mercury, and ultimately ends in death. When the dose is as large as 0.2 gram to the kilo the pulse becomes very slow, but is soon replaced by a stage of very rapid beating, which continues to death. The blood pressure rises about 20 mm. of mercury. The slowing of the pulse, which is seen after the use of 0.166 gram to the kilo, we have proved to be due to stimulation of the vagus nerves, since section of these nerves at once produces a rapid rate characteristic of vagal section in the normal animal. That this is not due in any way to the convulsions is proved by its occurrence in the curarised dog.

The fall of arterial pressure noted after the use of 0.166 gram to the kilo is due to the slowing of the pulse, since it was at once removed by section of the pneumogastric nerves, and the rise of pressure seen on the administration of 0.2 gram to the kilo is due to the increased force of the heart-beat, which is remarkably increased at this time. Further than this, the changes in the blood so interfere with its function as to produce asphyxia, thereby causing a rise of pressure. Finally, when the rapid pulse of the second stage is present, the pressure is kept up by this rapid pulse for a time, but ultimately falls, owing to the gradual paralysis of the vaso-motor system by reason of the gradual increasing asphyxia due to the changes in the blood and to the depression of the respiratory centre directly or indirectly. The cause of the rapid pulse seen during the second stage is pneumogastric palsy of a peripheral type, as powerful stimulation of these nerves fails to control the heart in the least. The lethal dose is about 0.08 to 0.1 gram to the kilo of the dog's weight by the jugular vein.

In the studies made by Brieger¹ upon the frog he found that the dose of 0.005 gram to a 55-gram frog caused convulsions in one minute, death in four and one-half hours; that 0.01 gram to a larger frog caused death in two and one-half hours, and

¹ Loc. cit.

that doses below 0.005 gram to 55 grams of frog produced death in six hours, while still smaller ones caused a fatal result in eight and one-half hours, convulsions only coming on in two hours. Brieger also found in a rabbit that the dose of about 0.0166 gram to the kilo given by the stomach produced no symptoms. On the next day he gave the same animal about 0.0332 gram to the kilo, and in half an hour cramps came on in the extremities. Along with these symptoms there was dilatation of the blood-vessels and lowered blood pressure with slowing of the pulse, which was soft and smaller, sensibility remained intact, and the reflexes at first increased, but failed later on. When smaller doses were given, less violent convulsions came on, but the urine was dark and contained no free hydroquinone.

According to Beyer,¹ small doses of hydroquinone in the frog reduce the rate of the heart and the amount of work done, and larger doses paralyse the walls of the great veins, sinus and auricles in the order in which they are named, while the ventricle is affected but slightly. In the heart of the terrapin small doses of hydroquinone slightly increase the work done by the heart, but reduce the pulse-rate, while larger doses decrease both rate and work. The sinus and auricle are much the most affected, the ventricle being least depressed. It first causes a contraction, then a dilatation of the veins, capillaries and arterioles, the veins being most affected. When injected into the body, muscular twitchings come on. It depresses the action of the red blood corpuscles. The blood becomes purplish brown. The drug acts more on veins than on arteries. It slows the pulse by acting on peripheral vagi. 0.1 to 0.2 gram to 100 cc. water acting on a 280-gram frog paralyses the veins and almost completely paralyses the ventricle. Brieger states that it produces dilatation of arterioles and lowered blood pressure. Small doses decrease the rate slightly; the pulse becomes small and soft.

It will be seen, on examining the results reached in our research, that they are in accord with those of the experimenters who have already worked with these drugs, and it may not be out of place to state that in those points where the results are not identical, the discrepancy lies in the fact that Beyer used the isolated heart of the frog and terrapin. It will be noted first of all that Brieger and ourselves have found (ortho) pyrocatechin the most poisonous of

¹ American Journal of Medical Sciences, April, 1886.

the group, hydroquinone also acting almost but not quite as powerfully, and the meta compound or resorcin proving itself the weakest of all. Thus in our work the lethal dose of pyrocatechin was found to be about 0.04 or 0.05 gram to the kilo; with hydroquinone it was found to be about 0.08 to 0.1 gram to the kilo, while resorcin was fatal only when the dose rose as high as from 0.7 to 1 gram to the kilo. In Brieger's studies the lethal dose of pyrocatechin was found to be 0.005 gram to 55 grams in the frog, death occurring in two hours, while with hydroquinone the same dose in the same kind of animal was followed by death in four and one-half hours. If the dose of pyrocatechin and hydroquinone was 0.01 gram to 55 grams, death came on in two hours with the former, and in two and one-half hours in the latter. The lethal dose of resorcin in the frog Brieger found to be 0.01 gram to 55 grams of frog's weight, only after six hours. 0.005 gram would not kill. In the research of Beyer it was found that hydroquinone was much more powerful than resorcin. Thus Beyer found that when a solution of hydroquinone of the strength of 0.5 to 500 cc. of saline was passed through the heart of a terrapin of 940 grams weight, a good deal of effect was felt, whereas a solution of 1 gram to 500 cc. of saline produced no effect. Again, Beyer found that it only required 0.4 gram of hydroquinone to 55 cc. of saline to kill the heart, whereas as much as 1 gram to 55 cc. was necessary if resorcin was used. He made no studies of pyrocatechin.

Phloroglucin.

When phloroglucin in the dose of 0.66 gram to the kilo is injected into the jugular vein of a dog attached to a manometer, through the carotid artery, it produces slowing of the pulse-rate by many beats and a slight fall of arterial pressure, which was but transient and which returns to the normal after a few seconds. The fall of pressure is very evidently due to the injection of the drug. That the slowness of the pulse is not due to cardiac depression seems proved by the absence of a fall of pressure, and by the fact that the pulse-waves are much increased in force. Section of the vagi only partially restores the rate of the pulse, and the slowing would seem to depend upon peripheral stimulation of these nerves, since the rate after section is still slower than it was before the dose was given. The blood under these circumstances does not show much, if any, change.

If the dose be as large as 0.8 gram to the kilo in 80 cc. of water, the pulse in the course of two minutes becomes slower by as much as 20 or 30 beats a minute, and a very marked fall of arterial pressure amounting to 60 mm. of mercury occurs, which is reduced by one-half as soon as the heart is rid of the drug. The slowing of the pulse is persistent and is not removed in the slightest by cutting the vagus nerves, so that, with these doses, as with the smaller ones, the peripheral vagi are stimulated, the pulse-waves being very full and strong.

The lethal dose to the dog by the jugular vein is between 1.0 gram and 1.2 gram to the kilo of his weight. Under such circumstances, death is due to respiratory failure, the heart beating some minutes after respiration ceases. That the action of the drug is on the respiration is also proved by the fact that the rapid injection of the compound into the jugular does not injure the heart. Whether the poison acts on the respiratory centre or not we cannot state, since the changes produced in the blood are noteworthy. Unlike pyrogallol, which produces remarkably black blood, this compound seems to make it more of a red-brick color or reddish brown, at the same time making it grumous looking or as a strong mixture of water-color paints appears. No struggles or convulsions come on with lethal doses, the animal passes so quietly from life to death as to make careful examination by the experimenter necessary before he can be absolutely certain that death has occurred.

Pyrogallol.

This substance when injected into the jugular vein of a dog in the dose of 0.05 gram to the kilo causes a slight increase of blood-pressure, due probably to gradual asphyxia and a pulse-rate which is somewhat slowed. The blood becomes exceedingly black in appearance and looks as dark as ink. No other symptoms are noted. If the dose be 0.1 gram to the kilo, a progressive fall of arterial pressure occurs until it reaches the abscissa line of the tracing about 8 minutes after the administration of the dose. The pulse is slowed by nearly one-half at this time, but is fairly strong, considering the exceedingly low arterial pressure. The change in the blood under such a dose is extraordinary, and death is brought about by failure of respiration, which ceases two or three minutes before the heart stops beating. That the fall of arterial

pressure is owing to a gradual asphyxia due to the altered blood is proved by the fact that artificial respiration in a curarised animal fails to maintain the pressure or put off death for any length of time. The lethal dose of pyrogallol by the jugular vein is from 0.08 to 0.1 gram to the kilo. There are no struggles whatever after poisonous doses, and no general symptoms, except those of weakness and intoxication with unconsciousness, appear.

The following summary shows the points of similarity and dissimilarity between these two substances. Both slow the pulse by vagal stimulation. Both change the appearance of the blood. Both kill by respiratory failure, direct or indirect. Pyrogallol is much the more poisonous, 0.05 gram to the kilo being equal to nearly 1 gram to the kilo of phloroglucin. Death from pyrogallol in the jugular vein is produced by from 0.08 to 0.1 gram to the kilo, from phloroglucin it is 1.0 to 1.2 gram to the kilo.

(To be continued.)

Contribution from the Chemical Laboratory of Clark University, Worcester, Mass.

ON TAUTOMERIC COMPOUNDS.

II.

By J. U. NEF.

The striking resemblance of ethyl dioxyterephthalate and of ethyl dioxypyromellithate as well as of ethyl succino-succinate and of ethyl *p*-diketo-hexam-ethylenetetracarboxylate to ethyl acetoacetate and ethyl benzoylacetate, must become apparent to any one who has worked with these compounds. Just as in the case of ethyl acetoacetate, metallic sodium acts on these substances with evolution of hydrogen and formation of readily soluble and unstable sodium salts.

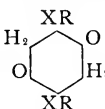
That in the case of ethyl acetoacetate the metal is bound to oxygen, thus, $\text{CH}_3-\text{CO}-\text{Na}=\text{CH}-\text{CO}_2\text{C}_2\text{H}_5$, has been made exceedingly probable by the recent experiments of Claisen.¹ Never-

¹ Ber. d. chem. Gesell. 20, 646, 651.

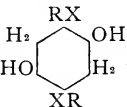
theless, on treatment of this salt with alkyl iodides, products are formed which unquestionably have the alkyl group bound directly to carbon, $\text{CH}_3 - \text{CO} - \text{CHR} - \text{CO}_2\text{C}_2\text{H}_5$, and not to oxygen, $\text{CH}_3\text{COR} = \text{CH} - \text{CO}_2\text{C}_2\text{H}_5$, as might be expected. The decomposition products¹ of substituted aceto-acetic ethers as well as their behavior towards hydroxylamine and phenylhydrazine leave no room for doubt that the alkyl group is bound directly to carbon.

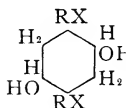
It was therefore of interest to determine whether the products formed by the introduction of alkyl as well as of acid radicals in the case of the above mentioned four compounds have the substituted radical (R) bound to carbon or to oxygen.

If, for instance, in the case of succino-succinic ether the alkyl

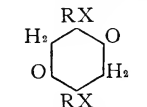
group (R) is bound to carbon, , the compound ob-

tained must show the behavior of a ketone, *i. e.* it must form a hydrazone or oxime, and must easily be converted by reducing

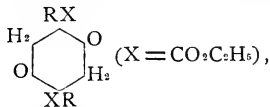
agents either into a phenol, , or secondary alcohol,

. Furthermore, the above ketone formula admits

of no chemical isomers, and of only two geometrical² isomers,



Cis-dialkyl derivative.



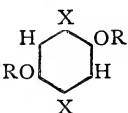
Trans-dialkyl derivative.

which it must be possible to convert one into the other.

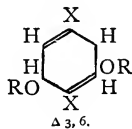
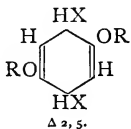
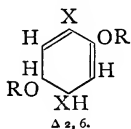
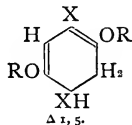
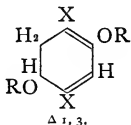
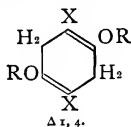
If, on the other hand, in the case of succino-succinic ether, the

¹ Wislicenus, Ann. Chem. (Liebig) **186**, 187.

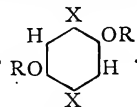
² v. Baeyer, Liebig's Annalen **245**, 169, 128.

alkyl group is bound to oxygen,  H₂, there are six¹

distinct chemical isomers possible according to the position of the two hydrogen atoms, namely :



These isomers are all to be considered as dihydro-benzene derivatives, and by removal of the two hydrogen atoms must all give

one and the same simple benzene derivative, 

These isomers must also show the behavior of phenol ethers and not be acted upon by either hydroxylamine or phenylhydrazine. Further, they cannot by addition of more hydrogen be converted into bodies acting like phenols or secondary alcohols.

The study of the substitution-products of the four above mentioned substances has conclusively proved that in all of them the substituted group is bound to oxygen. Their behavior is entirely in harmony with the above theoretical deductions, and the proofs are especially convincing in the case of succino-succinic ether.

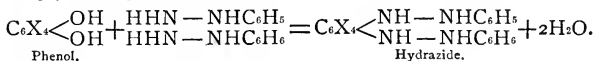
While only one dibenzyl-dioxyterephthalic ether was obtained, three simple isomeric and one polymeric dibenzyl succino-succinic ethers were obtained; also, whereas only one dibenzoyl-dioxyterephthalic ether was obtained, it was possible to isolate with

¹ There are more than six isomers possible if geometric isomers and isomers with para bonds be considered. The existence of the latter is, however, rendered exceedingly improbable by the work of v. Baeyer on the constitution of benzene, *Ann. Chem.* (Liebig) **245**, 112; *ibid.* **251**, 259.

certainly five isomeric dibenzoyl succino-succinic ethers; the latter are therefore to be regarded as dihydro-dibenzoyl-dioxy-terephthalic ethers; they all give on treatment with bromine in carbon disulphide solution one and the same dibenzoyl-dioxy-terephthalic ether.

These facts furthermore make it probable that ethyl succino-succinate itself is also nothing but a dihydro-dioxyterephthalic ether, which also v. Baeyer¹ has recently considered probable. This substance, however, is still regarded as tautomeric, just as also acetoacetic ether, phloroglucin, and many others; *i. e.* it seems to show a twofold chemical behavior, sometimes acting like a phenol, then again as a ketone. In order to explain the behavior of such tautomeric substances the assumption has to be made that according to the reagent acting upon them, the hydrogen is bound either to carbon or to oxygen. Such an explanation has unquestionably much against it, and especially since it attacks the foundation of modern structural chemistry it is of the utmost importance that the most convincing proofs be brought forward to justify it.

Since Jeanrenaud² has explained the reaction which takes place when hydroxylamine acts upon ethyl succino-succinic ether, there is not a single reaction which is in favor of the ketone or hexamethylene nature of this substance, except that with phenylhydrazine.³ This is no longer convincing, since also phenols with several electro-negative groups react with phenylhydrazine. In order to explain this reaction with phenols it is entirely unnecessary to make the assumption of a pseudo-form; the reaction simply takes place as follows:

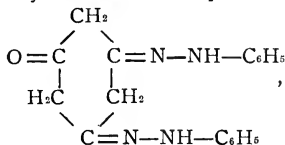


Phenol.

Hydrazide.

Water is split off and a hydrazide formed.

The recent paper of v. Baeyer and Kochendoerfer⁴ on the action of phenylhydrazine on phloroglucin is entirely in favor of this explanation. They did not obtain a hydrazone derivative,



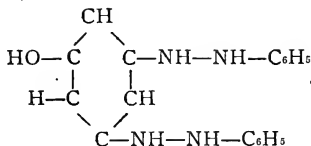
¹ Ann. Chem. (Liebig) **245**, 190.

³ Knorr and Bülow, Ber. d. chem. Ges. **17**, 2053.

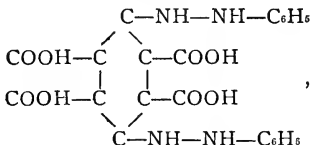
² Ber. d. chem. Ges. **22**, 1283.

⁴ Ber. d. chem. Ges. **22**, 2189.

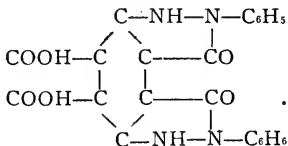
but a hydrazide,



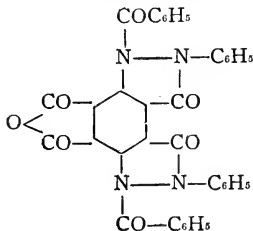
On the assumption of a pseudo-phloroglucin it is again necessary to assume a molecular rearrangement of a hydrazone to a hydrazide derivative. Furthermore, it has been proved that the reaction takes place in an analogous manner also in the case of another phenol, namely, hydroquinone-tetracarboxylic acid. There is formed at first a hydrazide,



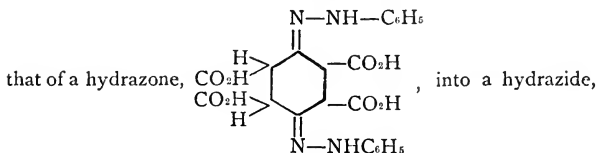
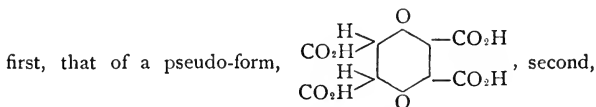
which instantly splits off water, giving the pyrazolon derivative,



This substance is converted by benzoyl-chloride into a dibenzoyl derivative, and at the same time anhydride formation takes place,

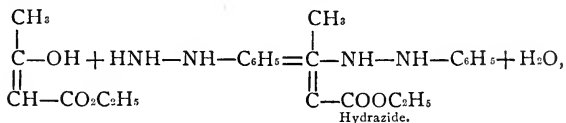


In order to explain these facts by the assumption of tautomerism a twofold molecular rearrangement has to be assumed,

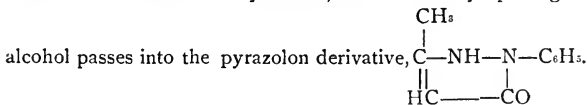


and this is hardly to be considered probable.

The above facts make it also probable that the pyrazolon derivatives as a whole cannot have the constitution last given them by Knorr.¹ The reaction, for instance, between phenylhydrazine and acetoacetic ether takes place as follows:

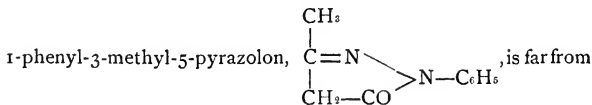


with the formation of a hydrazide, which then by splitting off



By this formula the formation of antipyrine can be explained in a very simple manner, since by the action of methyl iodide the hydrogen of the imide group is simply replaced by methyl.

The explanation of Knorr² for the formation of antipyrine from



probable.

¹ Ann. Chem. (Liebig) **238**, 149.

² Ann. Chem. (Liebig) **238**, 207.

For this reason experiments have been begun with phenylhydrazine as well as pyrazolon derivatives of acetoacetic ether and of succino-succinic ether, in order to determine whether the reaction in reality does take place just as above with phloroglucin and hydroquinone-tetracarboxylic acid.

Succino-succinic ether, as well as ethyl dioxyterephthalate, are therefore not tautomeric compounds; they react solely as phenol-like bodies. The different physical modifications of these substances correspond in no way to the assumed desmotropic conditions given them by Hantzsch and Herrmann¹; they are simply physical isomers. There are a vast number of organic compounds which crystallise in more than one modification, for instance, benzophenone, meta-dinitrobenzene, triphenylmethane, mandelic acid, and mercury diphenyl, where it is absolutely impossible that the different modifications correspond to chemically different compounds, and where even polymerism is excluded. Furthermore, in the course of the following investigation a number of substances have been discovered which appear in several crystalline forms, and where desmotropic conditions are entirely excluded. Thus, for instance, diacetyl succino-succinic ether crystallises in two different modifications (discovered by Dr. Muthmann); also ethyl β -benzoyl-dihydro-dioxyterephthalate appears in two, perhaps three, entirely distinct forms. In order to explain this by means of desmotropic conditions, the assumption would have to be made of a constant wandering of the benzoyl and acetyl group from oxygen to carbon and *vice versa*, which is furthermore entirely inconsistent with the chemical behavior of these substances.

The differences between the various forms in which a substance crystallises have unquestionably nothing to do with the chemical constitution, but are to be explained solely on physical grounds. The property of polymorphism is explained most simply by the different arrangement of the same molecules in the various crystalline forms.

The assumption of Hantzsch and Herrmann² that all benzene derivatives are colorless, while hydrogenated benzene derivatives are colored, is confuted by the following facts:

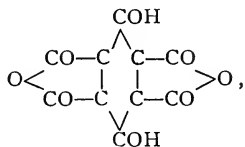
1. The diimido-derivative of ethyl *p*-diketo-hexamethylene-

¹ Ber. d. chem. Ges. **20**, 1303, 2801; **21**, 1754.

² Ibid.

tetracarboxylate is a *perfectly colorless* substance, in every way analogous in chemical behavior to the diimido-derivative of succino-succinic ether.¹ This substance, whether it be regarded as a diamido or diimido derivative, is either a dihydro- or a hexahydro-benzene derivative, and should therefore, according to the hypothesis of Hantzsch and Herrmann, be colored.

2. The *yellow colored* acids, dioxytterephthalic and dioxypyromellithic acid, are *undoubtedly benzene* derivatives. Their great stability in comparison to succinylo-succinic acid² can only be explained in this way; furthermore, the instability of the carboxylated derivatives of benzoquinone³ makes it probable that a carboxylated dihydro-quinone would be extremely unstable. Now, dioxypyromellithic acid on being heated to 300°–350° loses water and goes quantitatively into the dianhydride,



which can be distilled without decomposition. It is a deep dark yellow colored substance possessing a strong red fluorescence. On heating with acetic anhydride it is instantly converted into a colorless diacetyl derivative, which proves that it has two phenol hydroxyl groups, and therefore, *though strongly colored*, it is a *benzene derivative*. The salts of the hydroquinone dianhydride are *also colored deep red, almost black*.

3. The sodium salt of the primary methoxy-pyromellithic ether which crystallises in *yellow fluorescent plates*, and could be analysed, is a *benzene derivative*, $\text{C}_6 \left\{ \begin{array}{l} \text{ONa} \\ \text{OCH}_3 \\ (\text{CO}_2\text{C}_2\text{H}_5)_4 \end{array} \right.$, since on treatment with methyl iodide it is converted quantitatively into dimethoxy-pyromellithic ether, an unquestioned benzene derivative.

4. The disodic salt of dioxy-pyromellithic ether contains alcohol and is a reddish yellow substance. On driving off the alcohol, by

¹ v. Baeyer, Ber. d. chem. Ges. **19**, 428.

² Herrmann, Ann. Chem. (Liebig) **211**, 321; v. Baeyer and Noyes, Ber. d. chem. Gesell. **22**, 2168.

³ Ann. Chem. (Liebig) **237**, 1.

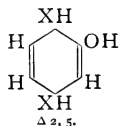
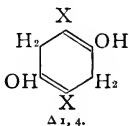
heating at 100° , it is converted into a *deep red powder* like vermilion. The substance is a *benzene derivative*, $C_6 \left\{ \begin{array}{l} (ONa)_2 \\ (CO_2C_2H_5)_4 \end{array} \right.$, since by treatment with benzoyl or acetyl chloride it can be converted almost quantitatively into the corresponding ether, which is undoubtedly a benzene derivative.

The remarks of Hantzsch and Herrmann¹ about the salts of dioxyterephthalic ether and of diamidoterephthalic ether are also confuted by (3) and (4). Hantzsch and Herrmann² have put forward as the only chemical proof for desmotropism in the succino-succinic series, the fact that tetraoxyterephthalic ether and quinone-dioxyterephthalic ether give with hydroxylamine, oximes. I have already pointed out in my first paper on this subject³ that these substances are not oximes, but oxyammonium salts. This supposition was found to be correct by Böniger,⁴ who again analysed the substances and found both identical and to be an oxyammonium salt.

There is therefore now absolutely no reason for assuming the existence of tautomerism or desmotropic conditions in the succino-succinic acid series. The polymorphism in this group is due to physical isomerism, just as has been so conclusively shown by Lossen⁵ to be the case with the hydroxamic acids.

As regards the constitution of succino-succinic ether, it might be expected that the five isomeric dihydro-dibenzoyl-dioxyterephthalic ethers would give by saponification five isomeric dihydro-dioxyterephthalic ethers. This is not the case, but succino-succinic ether was obtained from them all. The double bonds in these hydrogenated benzene derivatives must therefore wander and there exists only one stable condition. This is no longer surprising, since v. Baeyer⁶ has shown how easily this is the case with Δ 2, 5, Δ 1, 5, dihydroterephthalic acid.

Succino-succinic ether may be either Δ 1, 4⁷ or Δ 2, 5,



¹ Ber. d. chem. Ges. **21**, 1754.

² Hantzsch and Zeeckendorf, Ber. d. chem. Ges. **20**, 2799, 2800.

³ This Journal **11**, 5.

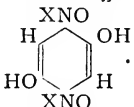
⁴ Ber. d. chem. Ges. **22**, 1289.

⁵ Ann. Chem. (Liebig) **252**, 170.

⁶ Ann. Chem. (Liebig) **251**, 290.

⁷ v. Baeyer, Ann. Chem. (Liebig) **215**, 190.

dihydro-dioxyterephthalic ether. The $\Delta 2, 5$ formula explains best the formation of dinitroso-succino-succinic ether,¹ which unquestionably has the two nitroso groups bound to the carbon atoms

holding $\text{CO}_2\text{C}_2\text{H}_5$, . Furthermore, the correspond-

ing dihydro-diamido-terephthalic ether (commonly known as the diimide of succino-succinic ether) belongs to the hexagonal trapezohedral, tetartohedral system,² and must therefore possess asymmetrical carbon atoms, which is only the case with the $\Delta 2, 5$ formula.

Remarkable is the fact that succino-succinic ether, as well as *p*-diketo-hexamethylene-tetracarboxylic ether, cannot be further reduced, which must undoubtedly be the case if these substances ever appeared as ketones. Since *p*-diketo-hexamethylene-tetracarboxylic ether is very stable in alkaline solution, attempts were made to add hydrogen by means of long treatment with sodium amalgam, but without success. Experiments in acid solution with zinc dust gave the same negative results.

If the hypothesis be made that hydrogen adds itself only with great difficulty to a carbon atom containing the hydroxyl group, $-\text{COH}=\text{}$, in a closed chain of carbon atoms, the above fact is explained without difficulty, whether the resulting compound be regarded as a $\Delta 1, 4$ or a $\Delta 2, 5$ dihydro-derivative. It is then also no longer surprising that monoxy-terephthalic acid³ takes up four hydrogen atoms and not two by treatment with reducing agents.

The above hypothesis is, however, only offered as a suggestion and little value is to be attached to it. The fact that *p*-dioxyterephthalic ether, as well as its acid and alcohol ethers, take up only two hydrogen atoms by reduction is beyond dispute.

The great resemblance of succino-succinic ether and of dioxyterephthalic ether to aceto-acetic ether makes it probable that also the last-named substance is a compound containing the hydroxyl group, $\text{CH}_3-\text{COH}=\text{CH}-\text{CO}_2\text{C}_2\text{H}_5$. This being the case, it ought also to form alkyl and acid ethers in which the substituted group (R) is bound to oxygen, $\text{CH}_3-\text{COR}=\text{}$

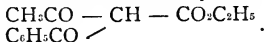
¹ Ann. Chem. (Liebig), **229**, 58.

² Muthmann, Zeitschr. für Kryst. **15**, 62.

³ v. Baeyer and Tutein, Ber. d. chem. Gesell. **22**, 2178.

$\text{CH}-\text{CO}_2\text{C}_2\text{H}_5$; these ethers must then of course be insoluble in alkalis.

The experiments just begun with aceto-acetic ether with this object in view have given the following result: Sodic aceto-acetic ether,¹ when treated with one molecule of acetyl or benzoyl chloride, is converted partly into a product which is insoluble in alkalis. The yield, however, is very poor. 80 grams of sodic aceto-acetic ether give, when treated with benzoyl chloride, about 13 grams of a wine-yellow oil, insoluble in alkalis, besides very much mono-benzoyl-aceto-acetic ether,²



The oil was purified as follows: To get rid of a slight amount of benzoyl chloride, it was allowed to stand with sodic hydrate for about ten hours, shaking thoroughly from time to time; traces of benzoic ether were driven over with steam, and then the residual oil again extracted with ether and washed with sodic hydrate; after distilling off the ether, previously dried with calcic chloride, there remained about 13 grams of oil. Attempts to distill it in a vacuum were fruitless, since decomposition takes place. It was therefore dried at 150° and analysed with the following result:

0.3422 gram substance gave 0.8908 gram CO_2 and 0.1615 gram H_2O .

	Theory for	
	$(\text{C}_6\text{H}_5\text{CO})_2\text{C}=\text{C}-\text{CO}_2\text{C}_2\text{H}_5$ $\text{CH}_3-\text{CO}-\diagup$	Found.
C	71.01	70.98
H	5.30	5.25

The substance is therefore to be regarded as a dibenzoyl-acetoacetic ether. Hitherto it has not been possible to introduce two acid radicals into the acetoacetic ether molecule, and the reaction in this case is best explained by the assumption of a disodium salt of acetoacetic ether. The oil is decomposed in the cold by alcoholic potash, concentrated sulphuric acid, and by bromine in chloroform solution. In all three cases about 0.8 gram to 1 gram of pure benzoic acid was obtained from 2 grams of the oil. The experiments with this substance, as well as with the

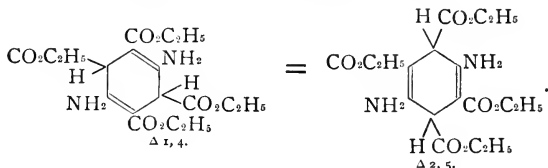
¹ Obtained by addition of sodium ethylate (free from alcohol) to aceto-acetic ether, diluted with an equal volume of absolute ether. The salt was dried on clay plates and washed with a small amount of ether, and then dried a short time at 100° .

² Bonne, Ann. Chem. (Liebig) 187, 1; E. Fischer & Bülow, Ber. d. chem. Gesell. 18, 2131.

product obtained by the action of acetylchloride upon sodic acetoacetic ether, will be continued.

EXPERIMENTAL PART.

Dihydro-diamido-pyromellithic ether,



On treating diamido-pyromellithic ether in alcoholic solution with zinc dust and dilute sulphuric acid, the chief product formed is para-diketo-hexamethylene-tetracarboxylic ether.¹ Besides this there is formed in small quantity an intermediate product,² which, since it is insoluble in caustic alkalies, can readily be separated from the main product. Diamido-pyromellithic ether is dissolved in as little hot alcohol as possible, a large excess of zinc dust, and then slowly dilute sulphuric acid (1 : 3) is added so as to cause a rapid evolution of hydrogen. As soon as the solution becomes colorless and a white crystalline precipitate begins to appear, a large amount of water is added and the mixture extracted with chloroform. The chloroform solution is washed with a 10 per cent. sodic carbonate solution, which takes up the saponified products, thereupon with dilute sodic hydrate, which extracts the diketone-compound with ease. The chloroform solution is washed with water and finally dried with calcic chloride; after distilling off the chloroform a white crystalline substance remains, which is difficultly soluble even in boiling alcohol, and crystallises therefrom in long fine needles, fusing at 212°.

0.1154 gram substance, dried at 110° and mixed with lead chromate, gave 0.2306 gram CO₂ and 0.0724 gram H₂O.

0.2015 gram substance, dried at 110°, gave 12.7 cc. nitrogen at 14° and 750 mm.

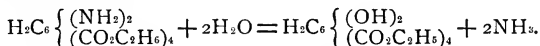
	Theory for $\text{H}_2\text{C}_6 \left\{ \begin{array}{l} (\text{NH}_2)_2 \\ (\text{CO}_2\text{C}_2\text{H}_5)_4 \end{array} \right\}$	Found.
C	54.40	54.50
H	6.54	6.97
N	7.04	7.41

¹Ann. Chem. (Liebig) **237**, 27.

²This Journal **11**, 7.

This same substance can also be obtained from para-diketo-hexamethylene-tetracarboxylic ether by melting with ammoniac acetate.¹ The yield in this case is very poor, and it is necessary to treat repeatedly with ammoniac acetate. The product finally dissolved in chloroform, and treated as above, was in every way identical with that obtained by reduction of diamido-pyromellithic ether.

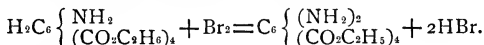
Dihydro-diamido-pyromellithic ether is a perfectly colorless substance; in solution it is easily oxidised and then attains a reddish color. It is most readily soluble in chloroform. On dissolving in concentrated sulphuric acid and adding a small amount of water, it is instantly converted into para-diketo-hexamethylene-tetracarboxylic ether,



The same ready elimination of the amido groups has been noticed by v. Baeyer in the case of the so-called diimido derivative of succino-succinic ether.

The stability of the imido groups in quinone diimido-pyromellithic ether,² where it is impossible under any condition to eliminate the nitrogen, is noteworthy in comparison with the above-mentioned dihydro-diamido-benzene derivatives, and leads to the conclusion that they must be very differently constituted.

On treatment of dihydro-diamido-pyromellithic ether, dissolved in concentrated sulphuric acid, with one molecule of bromine,¹ it is converted quantitatively, with evolution of hydrobromic acid, into diamido-pyromellithic ether, as follows:



The substance therefore shows in every respect a perfectly analogous behavior to diimido-succino-succinic ether. Remarkable, however, in a high degree is the fact that the substance is perfectly colorless, while diamido-pyromellithic ether, on the other hand, is colored deep red. Heated with acetic anhydride it is converted into a colorless acetyl derivative, melting at 132°.

Pyrazolon Derivative of Dioxy-pyromellithic Acid.

On treating hydroquinone-tetracarboxylic ether in alcoholic solution at 100° with phenylhydrazine, there is formed, as I have

¹ v. Baeyer, Ber. d. chem. Ges. **19**, 428.

² This Journal **11**, 5.

already shown, a dipyrazolon derivative.¹ Since this substance is very difficult to obtain in a pure state in large quantities, I began experiments with the free acid. On adding phenylhydrazine to an aqueous solution of dioxy-pyromellithic acid, a substance separates out on cooling in yellowish colored prisms which is nothing but a phenylhydrazine salt of the acid. On heating, this is converted into the dipyrazolon derivative. In order to obtain this compound it is best, however, to proceed as follows: To a hot aqueous solution of dioxy-pyromellithic acid twice the calculated amount of phenylhydrazine hydrochloride is added, and to complete the reaction the mixture is heated on a water-bath for three to five hours. Very soon a yellow crystalline granular product begins to separate out which is hardly at all soluble even in boiling water. After repeated washing with hot water the substance was obtained pure, as shown by the following analyses:

I. 0.1534 gram substance dried at 180° gave 0.3434 gram CO₂ and 0.0502 gram H₂O.

II. 0.2000 gram substance dried at 180° gave 0.4474 gram CO₂ and 0.0624 gram H₂O.

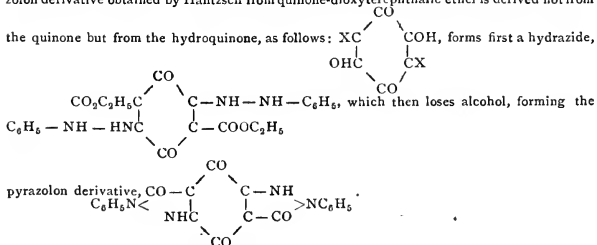
III. 0.1316 gram substance dried at 180° gave 15 cc. nitrogen at 14° and 756 mm.

	Theory for (CO ₂ H) ₂ C ₆ (^{NH} CO > NC ₆ H ₅) ₂ .	I.	Found.	II.
C	61.38	61.03		61.00
H	3.25	3.63		3.50
N	13.06	13.48		...

The dipyrazolon compound, therefore, unquestionably is derived from the hydroquinone and not from the quinone, as Hantzsch²

¹ This Journal **11**, 9.

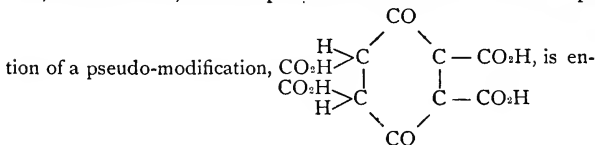
² Ber. d. chem. Ges. **22**, 2845. For the same reason it is extremely probable that the pyrazolon derivative obtained by Hantzsch from quinone-dioxyterephthalic ether is derived not from



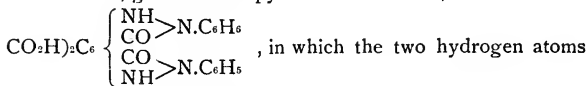
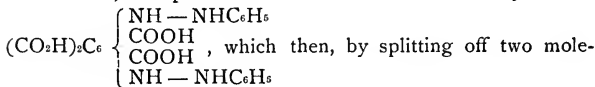
When one considers that it has not as yet been possible to obtain a hydrazone derivative from

believes, since a pyrazolon derivative containing two hydrogen atoms less requires only 2.80 per cent. hydrogen. The substance shows all the properties of a pyrazolon derivative; it dissolves in concentrated sulphuric acid, and on addition of water is precipitated unchanged; it dissolves in alkalis with deep purple coloration. The alkaline solutions, however, are readily oxidised, and on standing change in color to purplish red, reddish yellow, and finally to a stable yellow color showing a green fluorescence. The addition of an acid now precipitates a yellow amorphous flaky substance, which very likely is a compound containing two hydrogen atoms less, $[(\text{CO}_2\text{H})_2\text{C}_6(\text{CO} \xrightarrow{\text{N}} \text{N.C}_6\text{H}_5)_2]_x$. The same compound is obtained by oxidation of the alkaline solution with potassic ferricyanide, or better still by dissolving the pyrazolon derivative in fuming nitric acid and addition of water. The oxidation product is exceedingly stable; it can be boiled with alkalis without change, and even warm fuming nitric acid affects it but little.

The action of phenylhydrazine on hydroquinone-tetracarboxylic acid, it seems to me, can be explained best as follows: The assumption of a pseudo-modification,



is entirely unnecessary and, according to facts given in the theoretical introduction, is improbable. There is found at first a hydrazide,



are para quinone, and further that in case of the other anilic acids it is the hydroxyl group that is affected by hydroxylamine (this Journal 11, 21), it is extremely probable that the above explanation is the correct one.

In this connection I would again call attention to the fact that hydroxylamine and phenylhydrazine are decomposed by quinone tetracarboxylic ether with formation of the hydroquinone. This action is so energetic that even in the presence of much nitric acid reduction takes place.

bound to nitrogen are replaceable by metals and also readily removed by oxidation.

This, and at the same time the constitution of the pyrazolon derivative itself, is proved by the behavior of the latter towards benzoyl chloride. On heating this substance in a flask with an excess of benzoyl chloride, much hydrochloric acid is evolved. If thereupon the excess of benzoyl chloride be removed by shaking with sodic hydrate, there remains a yellow acid anhydride insoluble in alkalies. It is better, however, to convert the benzoyl chloride by heating with alcohol into benzoic ether, whereupon the anhydride, on cooling, separates out in crystalline yellow flakes. Recrystallised once from hot alcohol, in which it is readily soluble, the substance gave the following results on analysis:

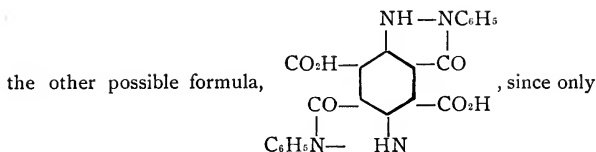
0.2067 gram substance dried at 110° gave 0.5271 gram CO₂ and 0.0705 gram H₂O.

Theory for $\text{O} < \begin{array}{c} \text{OC} \\ \text{OC} \end{array} > \text{C}_6\text{H}_5 \left\{ \begin{array}{l} \text{NCOC}_6\text{H}_5 \\ \text{CO} > \text{NC}_6\text{H}_5 \\ \text{CO} < \text{NC}_6\text{H}_5 \\ \text{N} > \text{COC}_6\text{H}_5 \end{array} \right.$			
C	69.68		Found. 69.54
H	3.23		3.78

It was possible to obtain good figures for carbon only by long ignition in a stream of oxygen, whereby the percentage of hydrogen found is somewhat high.

The dibenzoyl dipyrazolon anhydride melts at 140° to a viscous syrup, and volatilises without the slightest decomposition at a very high temperature. In solution, as well as in the solid state, it shows a green fluorescence. That the substance is an acid anhydride is proved by its behavior. After boiling an alcoholic solution with sodic hydrate, acids precipitate a yellow flaky substance which is readily soluble in alkalies, mild or caustic, and unquestionably represents the free acid while the benzoyl groups bound to nitrogen are not split off.

Benzoyl chloride has therefore acted on the dipyrazolon derivative as follows: first, the hydrogen atoms in the two imide groups are replaced by benzoyl, and at the same time anhydride formation has taken place between the two remaining carboxyl groups, which proves that the pyrazolon derivative cannot possess



phthalic acid, and not terephthalic acid, forms an anhydride.

Dioxy-pyromellithic acid is not affected by hydroxylamine under any other condition except the following: About ten times the calculated amount of hydroxylamine hydrochloride is added to a perfectly neutral solution of the potassium salt of the acid. After long boiling on a water-bath a yellow substance, crystallising in scales, separates out. It is completely insoluble in water and contains both potassium and nitrogen. On dissolving it in alkalis and pouring into a cold hydrochloric acid solution, a yellow granular product is precipitated which, on boiling with acids, is slowly converted into dioxy-pyromellithic acid.

The entire behavior of this substance proves that it is a hydroxamic acid like those obtained by Jeanrenaud¹ from acid ethers. It was therefore not further investigated.

Hydroquinone-tetracarboxylic Dianhydride, $(\text{OH})_2\text{C} \left(\begin{smallmatrix} \text{CO} \\ \text{CO} > \text{O} \end{smallmatrix} \right)_2$.

This substance is formed quantitatively by heating dioxy-pyromellithic acid for 10–15 minutes at 300°–350°. Water is given off in large amount, and finally at 350° the dianhydride begins to sublime. The deep yellow colored substance thus obtained is perfectly pure, as shown by analysis.

0.2187 gram substance gave 0.3866 gram CO_2 and 0.0182 gram H_2O .

	Theory for $(\text{OH})_2\text{C}_6 \left(\begin{smallmatrix} \text{CO} \\ \text{CO} > \text{O} \end{smallmatrix} \right)_2$.	Found.
C	48.00	48.22
H	.80	.92

The dianhydride is volatile without decomposition. The best solvent for it is dry acetone or acetic ether. Crystallised from the last-named solvent, it was obtained in yellow prisms which show a strong red fluorescence. It is slightly soluble in ether; if a trace of water be present the sides of the test-tube become colored

¹ Ber. d. chem. Ges. 22, 1270.

deep purple and blue. It dissolves in water at first with red color and yellowish red fluorescence; on standing or immediately on heating it goes over into dioxy-pyromellithic acid.

On heating with acetic anhydride it dissolves at first, but almost immediately the diacetyl-derivative, $C_6 \left\{ \begin{array}{l} (OCOCH_3)_2 \\ (CO > O)_2 \end{array} \right.$, separates

out in colorless pearly scales, which are very difficultly soluble in alcohol and ether, and are only slowly attacked by boiling water. Boiling with alkalis, however, converts the diacetyl derivative into dioxy-pyromellithic acid. It melts at a high temperature, and is volatile without decomposition.

The salts of the hydroquinone dianhydride are deep dark red in color, almost black; the potassium and ammonium salts were easily obtained by means of alcoholic potash and ammonia. Many attempts were made with these salts, as well as with the dianhydride itself, to obtain by oxidation quinone-tetracarboxylic dianhydride, $C_6 \left\{ \begin{array}{l} O_2 \\ (CO > O)_2 \end{array} \right.$, but without success.

On adding phenylhydrazine to an acetic ether solution of hydroquinone-tetracarboxylic dianhydride, there is formed at first a deep blue precipitate, which, on addition of more phenylhydrazine (in all 4 molecules), is converted into a yellow granular precipitate. Since this precipitate dissolves instantly in alkalis with yellow color and reddish fluorescence, and, on addition of acids, is precipitated again, the hydroxyl groups of the hydroquinone must have remained intact. The entire behavior of the product obtained shows that the anhydride groups have been attacked, and a product formed similar to those obtained by Hötte¹ with phthalic anhydride and phenylhydrazine.

Action of Halogens and of Nitric Acid on Dioxy-pyromellithic Acid.

On pouring bromine over hydroquinone-tetracarboxylic acid or its anhydride, not the slightest change is noticeable, even after many days. If, however, water be added, oxidation to the quinone and at the same time an evolution of carbonic anhydride take place. If the mixture be allowed to stand for twelve hours with an excess of bromine and some water, a yellow substance

¹ J. prakt. Chem. **35**, 265.

separates out in large quantity. Recrystallised from benzene, with addition of some alcohol, this was obtained in gold-yellow scales which melt at a high temperature and then sublime in scales. It coincides thus in its properties with bromanil.

0.1211 gram substance, dried at 110° , gave 0.0760 gram CO_2 and 0.0028 gram H_2O .

	Theory for $\text{C}_6\text{Br}_4\text{O}_2$.	Found.
C	16.98	17.12
H25

On treatment with caustic potash, it was converted into potassic bromanilate (obtained in long brownish red needles), and from it bromanilic acid was obtained with all its characteristic properties. The behavior of the bromanil towards nitrites¹ was studied, and potassic nitrilate obtained just as from chloranil. The potassium salt was converted into the barium, oxyammonium salt, as well as into nitrilic acid itself, and found to be in every way identical with the corresponding products from chloranil.

The bromanil was further converted by means of sulphurous acid in acetone solution into hydrobromanil. Recrystallised from acetic acid, this was obtained in long compact needles fusing at 246° .

A bromine determination according to the method of Carius gave the following results:

0.1361 gram substance, dried at 110° , gave 0.2428 gram AgBr or 0.1033 gram Br .

0.2951 gram substance, dried at 110° , gave 0.5202 gram AgBr or 0.2214 gram Br .

	Theory for $\text{C}_6\text{Br}_4(\text{OH})_2$.	I.	Found.	II.
Br	75.17	75.90		75.02

The formation of bromanil from hydroquinone-tetracarboxylic acid takes place in two stages. At first quinone-tetracarboxylic acid, $\text{C}_6 \left\{ \begin{smallmatrix} \text{O} \\ \text{(CO}_2\text{H)} \end{smallmatrix} \right\}_4$, is formed. The carboxylated derivatives of benzoquinone are, as I have already shown in the case of durylic acid quinone,² very unstable, and the carboxyl group is readily replaced by other groups, for instance, the nitro group.

In the second stage of the reaction, therefore, the bromine successively replaces all four carboxyl groups in quinone-tetracar-

¹ Ber. d. chem. Gesell., **20**, 2027.

² Ann. Chem. (Liebig) **237**, 17.

boxylic acid, and bromanil, $C_6Br_4O_2$, is thus formed. The yield of bromanil obtained is good; two grams acid gave regularly 1.1 gram bromanil.

On treatment of hydroquinone-tetracarboxylic acid with hydrochloric acid and potassic chlorate, there is likewise formed chloranil. The yield here too is a good one. The chloranil obtained was converted into hydrochloranil (fusing point found, 239°). It was also converted into potassic chloranilate and nitranilate. Since these substances, as well as the chloranil itself, were in every way identical with the corresponding products obtained from aniline, I deemed an analysis superfluous.

Iodine, potassium iodide and water do not act on hydroquinone-tetracarboxylic acid. On adding some iodic acid a violent reaction takes place, and a yellow substance is formed, which, however, is not iodanil, but iodoform.

From the above facts, and from the experience with durylic acid quinone, we should expect to obtain nitranil, $C_6(NO_2)_4O_2$, by the action of nitric acid on hydroquinone-tetracarboxylic acid. This, however, is not the case, but nitranilic acid is formed almost quantitatively. On adding hydroquinone-tetracarboxylic dianhydride in small portions to nitric acid (1.4) cooled to 0° , and then slowly adding an equal volume of water, nitranilic acid separates out in needles. It was purified according to the directions given in this Journal **II**, 18. The free acid, as well as the characteristic barium, sodium, potassium and oxyammonium salts, were compared side by side under the microscope with the corresponding products from chloranil, and found identical in every particular.

The above results with chlorine and bromine, as well as the results with durylic acid quinone, prove that unquestionably nitranil, $C_6(NO_2)_4O_2$, is at first formed. This substance, however, is extremely unstable, and immediately goes over into nitranilic

acid, $C_6 \begin{cases} (NO_2)_2 \\ (OH)_2 \\ O_2 \end{cases}$. I believe, therefore, that also by the action of nitrites on chloranil, nitranil is at first formed, but that it cannot be isolated.

A similar result was obtained by the action of potassic nitrite on quinone-dibromterephthalic ether. In this case also, not quinone-dinitro-terephthalic ether, but quinone-dioxy-terephthalic ether was obtained.

The above results confirm also the assumption of Nietzki and Preusser,¹ who found it necessary to suppose the intermediary formation of nitranil in order to explain the formation of nitranilic acid from meta-dinitro derivatives.

The behavior of dioxy-pyromellithic acid towards reducing agents is interesting. Many experiments carried on in acid and in alkaline solution showed that it was impossible to add hydrogen and at the same time prevent the splitting off of the carboxyl groups. The method by which para-dioxyterephthalic acid has been reduced² is here of no avail.

Also attempts to saponify dihydro-dioxy-pyromellithic ether (formerly called para-diketo-hexamethylene-tetracarboxylic ether), whether in alkaline or acid solution, proved that, notwithstanding all possible precautions, it was impossible to prevent the splitting off of the carboxyl groups as carbonic anhydride. The above ether, furthermore, is exceedingly stable in the presence of alkalis; it can, for example, be left in sodic hydrate solution for four days without much change.

These facts, as well as even more the results with succino-succinic acid,¹ show how unstable hydrogenated hydroxylised benzene-carboxylic acids are. Under these circumstances the knowledge of the great stability of dioxyterephthalic acid, and still more of dioxy-pyromellithic acid, leads one to the inevitable conclusion that these are *colored benzene derivatives*, and that they *can never exist* as dihydroquinone-carboxylic acids.

Attempts to prove whether the substituted groups in Dioxy-pyromellithic and in Para-diketo-hexamethylene-tetracarboxylic Ether are bound to Carbon or to Oxygen.

The first experiments on this subject have already been published in this Journal, Vol. 11, p. 1. The behavior of dimethoxy-pyromellithic ether (melting point 95°) proves that the methyl groups in it are bound to oxygen, since it reacts neither with phenylhydrazine nor hydroxylamine, and is not affected by bromine. Later experiments show that it can be treated with zinc dust and acetic acid without any change. In order to prove that the substance is a phenol ether, the following experiment was carried out: 4 grams dimethoxy-pyromellithic ether (melting point 95°) were heated in dilute alcoholic solution with one and a

¹ Ber. d. chem. Gesell. 20, 799.

² v. Baeyer and Noyes, Ber. d. chem. Gesell. 22, 2168.

half times the calculated amount of caustic soda. After evaporation of the alcohol, a white sodium salt was obtained which is little soluble in alcohol. A small portion was dissolved in water, and converted by means of lead acetate into the insoluble lead salt. This, after thorough washing, was decomposed by sulphuretted hydrogen, and the concentrated filtrate gave, on addition of concentrated hydrochloric acid, a colorless white substance, crystallising in needles, and exceedingly soluble in cold water. It in all probability is dimethoxy-pyromellithic acid. The main portion of the above sodium salt was converted into the colorless insoluble silver salt, which, treated with methyl iodide, gave in considerable quantity methyl dimethoxy-pyromellithate (melting point 134°), identical with the product described below. These facts prove conclusively that the methyl groups are bound to oxygen.

Further, the intermediate product¹ obtained by the action of methyl iodide on disodic dioxy-pyromellithic ethyl ether was analysed. It crystallises from alcohol in beautiful yellow plates showing a strong green fluorescence.

0.2200 gram substance, dried at 110° and mixed with lead chromate, gave 0.4188 gram CO_2 and 0.1069 gram H_2O .

0.1122 gram substance dried at 110° gave on ignition with H_2SO_4 0.0183 gram Na_2SO_4 .

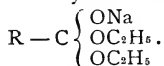
	Theory for $\text{C}_6 \left\{ \begin{array}{l} \text{ONa} \\ \text{OCH}_3 \\ (\text{CO}_2\text{C}_2\text{H}_5)_4 \end{array} \right.$	Found.
C	52.53	51.91
H	5.30	5.40
Na	5.30	5.29

The salt is but little soluble in water; the best solvent is alcohol, and the solution shows a greenish yellow fluorescence. It decomposes at high temperature without melting, and when treated with methyl iodide is converted quantitatively into dimethoxy-pyromellithic ether. On adding dilute sulphuric acid the salt is converted into a yellow oil which has a green fluorescence, is volatile without decomposition, and not acted upon by concentrated nitric acid. Sodid hydrate converts it back to the yellow sodium salt again, and it therefore must be $\text{C}_6 \left\{ \begin{array}{l} \text{OH} \\ \text{OCH}_3 \\ (\text{CO}_2\text{C}_2\text{H}_5)_4 \end{array} \right.$; it could under no condition be brought into the solid state.

¹ This Journal 11, 12.

The preparation of the sodium salts, especially of para-diketo-hexamethylene-tetracarboxylic ether, and of succino-succinic ether, can be accomplished with success only by following very definite conditions, just as in the case of acetoacetic ether.¹

There is a great tendency in these compounds, because of the presence of double bonds, to form addition products with sodium ethylate. Furthermore, Claisen² has shown that acid ethers, $R-CO_2C_2H_5$, also form addition products with sodium ethylate whereby the carboxyl group is changed to an ortho derivative,



If, for instance, a benzene solution of para-diketo-hexamethylene-tetracarboxylic ether be added to a benzene solution containing about ten times the calculated amount of sodium ethylate, no salt is precipitated at all, whereas this is the case if only the calculated amount (2 molecules) of sodium ethylate be present. On addition, however, of absolute ether, a white salt separates out which contains all the diketo compound used, and is readily soluble in water and reacts with bromine just as the disodic salt.³ The analysis showed that it contains 27.02 per cent. of sodium, which proves that much sodium ethylate is present simply as an addition product.

The sodium salts can, however, be obtained tolerably well by the following method, which was employed in the case of all the sodium salts made:

The substance is dissolved in dry chloroform; the calculated amount of sodium (two atoms) dissolved in as little alcohol as possible, and the solution, after cooling, diluted with chloroform, and immediately poured into the chloroform solution of the substance, taking care to shake thoroughly. In this way there is always formed fully 85 per cent. disodic salt and very little mono-sodic salt. The salts come down mostly as gelatinous precipitates, very difficult to filter. They were dried on clay plates, and when air-dried they contain up to 20 per cent. crystalline alcohol, which in most cases was easily driven off by heating at 100° in an air-bath.

¹ Wislicenus, *Ann. Chem. (Liebig)* **186**, **187**.

² *Ber. d. chem. Gesell.* **20**, 646.

³ *This Journal* **11**, 17.

Methyl Dimethoxy-pyromellithate, $C_6 \left\{ \begin{matrix} (OCH_3)_2 \\ (CO_2CH_3)_4 \end{matrix} \right.$.

The disodium salt of methyl dioxy-pyromellithate is precipitated as a yellow granular crystalline powder. On drying at 90° , it loses its crystal alcohol and becomes deep cinnabar red in color.

Over 85 per cent. of it is then $C_6 \left\{ \begin{matrix} (ONa)_2 \\ (CO_2CH_3)_4 \end{matrix} \right.$, as shown by the yield of diacetyl derivative obtained from it with acetyl chloride (see below). It dissolves in water with yellow color and with green fluorescence. On heating it in a sealed tube with an excess of methyl iodide it is converted into the dimethoxy-derivative. After distilling off the excess of methyl iodide, dilute sodic hydrate is added, and the emulsion obtained extracted with chloroform, and this then dried with calcic chloride. There is left, after distilling off the chloroform, a white product, which, crystallised once from methyl alcohol, is obtained in colorless rhombic plates melting at 134° .

0.1552 gram substance gave 0.2951 gram CO_2 and 0.0720 gram H_2O .

	Theory for $C_6 \left\{ \begin{matrix} (OCH_3)_2 \\ (CO_2CH_3)_4 \end{matrix} \right.$	Found.
C	51.89	51.86
H	4.87	5.16

The compound is volatile without decomposition; it is not acted upon by phenylhydrazine, hydroxylamine, or bromine. Long treatment with zinc dust in acetic acid solution is without effect. The solutions of the substance are colorless, and give no coloration with ferric chloride. Reduced in alcoholic solution with zinc dust and concentrated hydrochloric acid, it is converted into a hydrogenated benzene derivative, insoluble in alkalis, which was obtained as a colorless oil and could not be made to solidify.

Methyl Diacetyl-dioxy-pyromellithate, $C_6 \left\{ \begin{matrix} (OCOCH_3)_2 \\ (CO_2CH_3)_4 \end{matrix} \right.$.

This substance is formed instantly in the cold on adding acetyl chloride to the above mentioned sodium salt. The yield obtained was always 75–85 per cent.

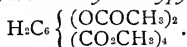
After extracting with chloroform, washing with alkalis, and evaporating the dried chloroform solution, the residue, crystallised once from methyl alcohol, was pure.

0.1276 gram substance, dried at 120°, gave 0.2378 gram CO₂ and 0.0516 gram H₂O.

	Theory for C ₆ { (OCOCH ₃) ₂ / (CO ₂ CH ₃) ₄ .	Found.
C	50.70	50.82
H	4.23	4.49

The diacetyl derivative is volatile without decomposition; it melts at 147°, and dissolves easily in hot methyl alcohol, crystallising therefrom in long silky needles. A chloroform solution of the substance is not affected by an excess of bromine, even on standing for many days. Concentrated sulphuric acid decomposes it instantly in the cold, with formation of acetic acid and dioxy-pyromellithic ether (melting point 207°). An alcoholic solution, treated with sodium ethylate, is converted into acetic ether and disodic dioxy-pyromellithic ether. The behavior of the compound is thus entirely that of an acid ether of a phenol. Although very unstable in alcoholic solution towards alkalis, it is stable towards concentrated hydrochloric acid, and therefore it was possible to convert it by reducing agents into a hydrogenated benzene derivative.

Methyl Dihydro-diacetyl-dioxy-pyromellithate,



The diacetyl-dioxy-pyromellithic ether is dissolved in as little hot methyl alcohol as possible, and an excess of zinc dust and concentrated hydrochloric acid is added slowly, so as to produce a very energetic evolution of hydrogen. In 5-10 minutes the reduction is completed. The solution is decanted from the zinc dust and poured into a large amount of water. After extracting with chloroform, washing first with sodic hydrate and then with water, the chloroform solution is dried with calcic chloride. The chloroform is then distilled off, and the residue obtained pure by repeated crystallisation from methyl alcohol.

0.1635 gram substance, dried at 110°, gave 0.3031 gram CO₂ and 0.0713 gram H₂O.

	Theory for H ₂ C ₆ { (OCOCH ₃) ₂ / (CO ₂ CH ₃) ₄ .	Found.
C	50.47	50.59
H	4.67	4.85

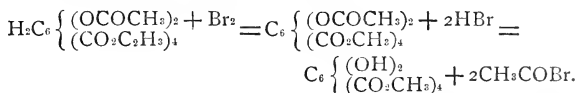
A dihydro-benzene derivative has therefore been formed, and it is impossible, even by repeated treatment with zinc dust and con-

centrated hydrochloric acid in alcoholic solution, to add more than two hydrogen atoms.

The substance is volatile without decomposition; it is dimorphous. Crystallised from a large amount of methyl alcohol (in which it is very much more difficultly soluble than the compound containing two hydrogen atoms less), it separates out, provided the solution is cooled slowly and without disturbance, in long needles. These are very unstable, and are easily converted into the stable or ordinary modification. This latter form is generally obtained by crystallisation from methyl alcohol as a porous, lustreless white powder, melting at 173° .

Concentrated sulphuric acid decomposes it in the cold into acetic acid and para-diketo-hexamethylene-tetracarboxylic ether (melting point 175°). Sodium ethylate (two molecules) saponifies it to acetic ether and the disodic salt of the diketo compound.

The substance dissolved in *anhydrous* ether is converted by the vapors of *dry* bromine (one molecule), notwithstanding all care, into dioxy-pyromellithic ether (melting point 207°) with evolution of hydrobromic acid. The nascent hydrobromic acid must therefore split off the acetyl groups as follows:



That this actually is the case is proved by the study of the corresponding dibenzoyl derivative where the benzoyl groups, because more stable, are not split off.

Treated with concentrated nitric acid (1.4) in the cold, the dihydro-diacetyl compound is converted first into dioxy-pyromellithic ether and then into quinone-pyromellithic ether (melting point 208°). Para-diketo-hexamethylene-tetracarboxylic ether itself shows exactly the same behavior with nitric acid.

The *same dihydro-diacetyl derivative* is formed by treating the sodium salt of para-diketo-hexamethylene-tetracarboxylic ether with acetyl chloride. Reaction takes place instantly in the cold, and after extraction with chloroform, washing with alkalies, etc., as above, a colorless substance was obtained (yield 20-40 per cent.). Recrystallised from methyl alcohol, it was obtained in needles or as a porous white powder melting at 173° , and thus, as well as in its chemical properties, it is identical with the product obtained by

reduction. Thereby it is conclusively proved that the substitution products of para-diketo-hexamethylene-tetracarboxylic ether have the substituted group (R) bound to oxygen,

$\text{H}_2\text{C}_6 \left\{ \begin{array}{l} (\text{OR})_2 \\ (\text{CO}_2\text{C}_2\text{H}_5)_4 \end{array} \right.$, and that these are dihydro-benzene derivatives.

Dibenzoyl-dioxy-pyromellithic ether, $\text{C}_6 \left\{ \begin{array}{l} (\text{OCOC}_6\text{H}_5)_2 \\ (\text{CO}_2\text{C}_2\text{H}_5)_4 \end{array} \right.$.

This compound is formed with a yield of 85–90 per cent. on treating disodic dioxy-pyromellithic ether with benzoyl chloride. It is, however, unnecessary to isolate the sodium salt. Ethyl dioxy-pyromellithate is dissolved in sodic hydrate and the solution shaken with benzoyl chloride.¹ The reaction is completed in five minutes, and the yield is 90 per cent. or over.

Recrystallised once from alcohol the product is pure.

0.2105 gram substance, dried at 110° , gave 0.4842 gram CO_2 and 0.0962 gram H_2O .

	Theory for $\text{C}_6 \left\{ \begin{array}{l} (\text{OCOC}_6\text{H}_5)_2 \\ (\text{CO}_2\text{C}_2\text{H}_5)_4 \end{array} \right.$	Found.
C	63.36	62.75
H	4.95	5.08

The dibenzoyl derivative crystallises from alcohol in rhombic colorless plates, melting at 157° . It can be obtained by crystallisation from acetic ether in transparent many-sided crystals, easily capable of goniometric measurement. It is not acted upon by concentrated nitric acid or on long standing with an excess of bromine in chloroform solution. Concentrated sulphuric acid saponifies it in the cold to benzoic acid and dioxy-pyromellithic ether. Alkalies in alcoholic solution also saponify it with formation of benzoic ether and the sodium salt of dioxy-pyromellithic ether. Reduced in alcoholic solution with zinc dust and hydrochloric acid, hydrogen is added and there is formed

Dihydro-dibenzoyl-dioxy-pyromellithic ether, $\text{H}_2\text{C}_6 \left\{ \begin{array}{l} (\text{OCOC}_6\text{H}_5)_2 \\ (\text{CO}_2\text{C}_2\text{H}_5)_4 \end{array} \right.$.

The method of preparation and purification of this substance is exactly like that described for the corresponding dihydro-diacetyl derivative. It crystallises from alcohol in long flat plates; from acetic ether in prisms, melting at 135° , and capable of goniometric measurement.

¹ Udransky and Baumann, Ber. d. chem. Gesell. 21, 2744.

0.2366 gram substance, dried at 110° , gave 0.5438 gram CO_2 and 0.1132 gram H_2O .

Theory for $\text{H}_2\text{C}_6 \left\{ \begin{array}{l} (\text{COC}_6\text{H}_5)_2 \\ (\text{CO}_2\text{C}_2\text{H}_5)_4 \end{array} \right.$		Found.
C	63.16	62.70
H	5.26	5.33

The substance is volatile without decomposition. It is a dihydro-benzene derivative, and it remains unchanged by long and violent treatment with zinc dust and hydrochloric acid (in alcoholic solution). Treated with 2 atoms of bromine in dilute carbon disulphide solution it is converted quantitatively, with evolution of hydrobromic acid, into dibenzoyl-dioxy-pyromellithic ether (melting point 157°). Concentrated sulphuric acid splits it in the cold into benzoic acid and para-diketo-hexamethylene-tetracarboxylic ether (melting point 143°). These two substances can easily be separated by means of hot water. A similar decomposition takes place with 2 molecules of sodium ethylate, forming benzoic ether and the sodium salt of the diketone compound.

This *same substance* now is formed on treating the sodium salt of para-diketo-hexamethylene-tetracarboxylic ether with benzoyl chloride. Noteworthy is the fact that no reaction takes place until the benzoyl chloride is heated to its boiling point.

The yield is a very good one: from 1 gram sodium salt, 0.6 gram pure dihydro-dibenzoyl derivative was obtained. The substance is identical in every way with the one obtained by reduction of dibenzoyl-dioxy-pyromellithic ether. The absolute physical identity is established by the following crystallographical results obtained by Dr. W. Muthmann:

Monoclinic system: $\beta = 52^{\circ} 37'$.

$$a : b : c = 1.8824 : 1 : 2.5039.$$

Planes: $r = (101) = -P_{\infty}$. $\rho = (\bar{1}01) = +P_{\infty}$. $a = (100) = +P_{\infty}$. $m = (110) = \infty P$. $q = (011) = P_{\infty}$.

Elongation in the direction of the axis b . The ortho-pinacoid appears as a small plane. The clinodome is sometimes absent.

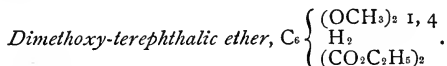
	Calculated.	Found.	
		Product from disodium salt.	Product obtained by reduction.
$m : m = (110) : (\bar{1}\bar{1}0)$	$112^{\circ} 28'$
$q : q = (011) : (0\bar{1}\bar{1})$	$126^{\circ} 38'$
$a : q = (100) : (011)$	$74^{\circ} 11'$

	Calculated.	Found.	
		Product from disodium salt.	Product obtained by reduction.
a : r = (100) : (101)	22° 18'	22° ½'
r : ρ = (101) : (101)	110° 0	110° 20'
ρ : a = (101) : (100)	47° 42'	47° ½'
m : r = (110) : (101)	59° 3'	58° 51'
r : q = (101) : (011)	67° 11'
q : m = (011) : (110)	53° 46'
m : ρ = (110) : (101)	68° 2'
ρ : q = (101) : (011)	85° 23'
q : m = (011) : (110)	26° 35'	26° 22'

The crystals are colorless and transparent. The plane of the optic axes is parallel to the plane of symmetry. An optical axis appears at an angle not far from the perpendicular to one of the hemidome planes. Double refraction is medium. The identity of the two products is therefore proved."

The above results with the diacetyl and dibenzoyl derivatives prove that the substituted group is bound to oxygen, as well in case of dioxy-pyromellithic ether as also in the case of paradiketo-hexamethylene-tetracarboxylic ether. Since the ethers of the last-named substance show in every way an analogous behavior, it becomes very probable that this substance itself is nothing but a dihydro-dioxy-pyromellithic ether, $H_2C_6 \left\{ \begin{array}{l} (OH)_2 \\ (CO_2C_2H_5)_4 \end{array} \right.$.

Attempts to prove whether the substituted groups in dioxy-terephthalic ether and in succino-succinic ether are bound to oxygen or to carbon.



The disodic salt of dioxyterephthalic ether contains, dried in a desiccator, 20 per cent. of alcohol, and is colored reddish yellow. It is not possible to obtain it free from alcohol. On heating at 100° it is decomposed to a grayish powder. The presence of the alcohol, however, is not a hindrance in the preparation of the ethers.

Twenty grams were heated with an excess of methyl iodide in a sealed tube at 100° for six hours. After extracting with chloroform, washing with sodium hydroxide, etc., as with all the ethers, there

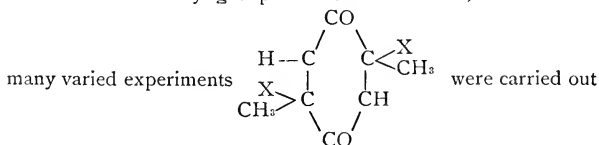
were obtained 14.5 grams of pure dimethoxy-terephthalic ether, instead of 15.2 grams calculated. Recrystallised from alcohol, it was obtained in colorless rhombic plates melting at 101.5° , and volatile without decomposition.

0.2066 gram substance, dried at 110° , gave 0.4500 gram CO_2 and 0.1179 gram H_2O .

	Theory for $\text{C}_8 \begin{cases} (\text{OCH}_3)_2 \\ \text{H}_2 \\ (\text{CO}_2\text{C}_2\text{H}_5)_2 \end{cases}$	Found.
C	59.57	59.39
H	6.38	6.34

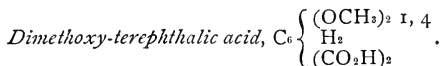
This substance shows a remarkably strong blue-violet fluorescence, which is deceptive and might lead one to call the substance colored. Large transparent, easily measurable crystals from acetic ether show, however, not the slightest coloration under the microscope in polarised light (Dr. Muthmann). The solutions of the substance also show a marked blue-violet fluorescence, but give no coloration with ferric chloride.

These physical properties of the substance are so very remarkable, since all the other ethers, as well in the succino-succinic as in the para-diketo-hexamethylene-tetracarboxylic ether series, show not the slightest trace of fluorescence. I was for a long time inclined to ascribe the fluorescence to the presence of an impurity, but notwithstanding all efforts by chemical means, as well as repeated recrystallisation, it was impossible to eliminate or weaken the fluorescence. It might, however, be possible that in this case the methyl groups are bound to carbon, and therefore



with phenylhydrazine and hydroxylamine, but without success. The substance remains unchanged on long digestion with zinc dust and acetic acid. Its entire behavior thus shows that the methyl groups are bound to oxygen. On standing with bromine in chloroform solution, it is unchanged; on heating, however, to 100° in a sealed tube, hydrobromic acid is evolved and a colorless non-fluorescent product formed, which crystallises in needles and melts at 128° . On reducing in alcoholic solution with zinc dust

and concentrated hydrochloric acid, hydrogen is added, and a colorless oil, insoluble in alkalis, is formed, which could not be made to solidify or be converted back into the original product.

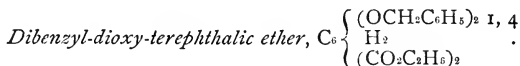


The sodium salt of this acid is formed quantitatively from the ether by heating for half an hour in dilute alcoholic solution with sodium hydroxide. After driving off the alcohol, the solution is poured slowly into dilute hydrochloric acid, whereby the free acid separates out almost completely as a white powder. Recrystallised twice from hot water (four grams require about a liter of boiling water for solution), it was obtained in long colorless needles melting at 265° .

0.2318 gram substance, dried at 150° , gave 0.4512 gram CO_2 and 0.0936 gram H_2O .

	Theory for $C_6 \left\{ \begin{array}{l} (OCH_3)_2 \\ H_2 \\ (CO_2H)_2 \end{array} \right.$	Found.
C	53.10	53.08
H	4.42	4.53

Just as is the case with the ether, an aqueous solution of the acid shows a marked blue-violet fluorescence, which is not destroyed by mineral acids; ferric chloride causes not a trace of coloration, nor does it affect the fluorescence in the least. In the solid state, the acid, however, shows no fluorescence. Also the salts of the acid are colorless, and the solution of the ammonium salt shows no fluorescence. The silver salt is soluble in hot water, and crystallises therefrom in long, flat, radiating needles. The lead salt separates out in flakes, which quickly settle and transform themselves into a white granular powder.



Since by the reduction of dimethoxy-terephthalic ether, as well as from disodic succino-succinic ether and methyl iodide, oily products are obtained which cannot be made to solidify, experiments were undertaken with the benzyl ethers. On heating disodic dioxyterephthalic ether with an excess of benzyl chloride

for about one to two hours with reversed condenser, reaction takes place. In order to be certain that no molecular rearrangement has taken place, an experiment was carried out with benzyl iodide, which reacts on the sodium salt at 100° . In both cases exactly the same compound is formed. When the reaction is completed the excess of benzyl chloride is distilled off by heating in a metal bath to 230° . The residue is extracted with chloroform, washed with sodium hydroxide, etc., and then recrystallised from alcohol, whereby it is separated from the benzyl chloride still left.

10 grams salt gave, when treated with benzyl chloride, 5 grams ether.

5 grams salt gave, when treated with benzyl iodide, 2.8 grams ether.

The product obtained with benzyl chloride is always colored slightly yellow; treated with zinc dust in acetic acid solution, it can, however, be obtained entirely colorless, as is the case directly with the product obtained by means of benzyl iodide. Recrystallised from alcohol, in which it is very easily soluble when hot, the ether is obtained in needles, melting at 96.5° .

0.2096 gram substance, dried at 110° , gave 0.5494 gram CO_2 and 0.1146 gram H_2O .

	Theory for $\text{C}_6 \left\{ \begin{array}{l} (\text{OCH}_2\text{C}_6\text{H}_5)_2 \\ \text{H}_2 \\ (\text{CO}_2\text{C}_2\text{H}_5)_2 \end{array} \right\}$	Found.
C	71.89	71.54
H	5.99	6.10

As the methyl ether this substance is colorless; it shows, however, a blue-violet fluorescence. The alcoholic solution also shows a marked blue-violet fluorescence, but it gives no coloration with ferric chloride. I am indebted to the kindness of Dr. W. Muthmann for the following description of the optical properties of this compound: "Needles, belonging to the monoclinic system, elongated in the direction of the axis of symmetry. The plane of the optic axes is perpendicular to the plane of symmetry, and forms with the normal to the predominant ortho plane a not very large angle. The acute bisectrix comes out at an angle through the mentioned predominant ortho plane (in sodium light). The axial angle is too great, so that the axes are not visible under the microscope."

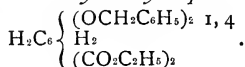
The substance is volatile without decomposition; it is not acted upon by hydroxylamine or phenylhydrazine, or by reduction

with zinc dust in acetic acid solution. The benzyl groups are stable in the presence of alkalies, so that on saponifying with alcoholic potash, a colorless acid, insoluble in water, is obtained which is probably dibenzyl-dioxy-terephthalic acid. In the presence of acids, however, the benzyl groups are less stable, and by boiling in alcoholic solution with concentrated hydrochloric acid the substance is converted into dioxy-terephthalic ether (melting point 133°).

Bromine, in chloroform solution, already attacks the substance in the cold with evolution of hydrobromic acid. A yellow substance crystallising from alcohol in flat needles, melting at 132° , was obtained, and it is probable that the bromine has attacked the benzyl groups, substituting the hydrogen atoms.

By reduction in alcoholic solution with zinc dust and concentrated hydrochloric acid, a dihydro-benzene derivative is formed, namely :

α -Dihydro-dibenzyl-dioxyterephthalic ether,



The yield by the reduction is a very poor one, about 5 per cent., because of the instability of the benzyl groups in acid solution. It is essential to have a violent evolution of hydrogen and not to heat longer than five minutes, otherwise products, soluble in alkalies, are obtained, which are succino-succinic ether and dioxy-terephthalic ether.

After extracting with chloroform, washing with alkalies, etc., a product is obtained which is very difficultly soluble, even in boiling alcohol, and crystallises therefrom in colorless needles, melting at 169° ; in solution these show a very weak blue-violet fluorescence, which cannot be removed.

0.1677 gram substance, dried at 110° , gave 0.4404 gram CO_2 and 0.0994 gram H_2O .

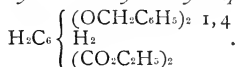
	Theory for $\text{H}_2\text{C}_6 \left\{ \begin{array}{l} (\text{OCH}_2\text{C}_6\text{H}_5)_2 \\ \text{H}_2 \\ (\text{CO}_2\text{C}_2\text{H}_5)_2 \end{array} \right.$	Found.
C	71.56	71.62
H	6.42	6.62

The substance is volatile without decomposition; by boiling in alcoholic solution with concentrated hydrochloric acid, the benzyl

groups are easily split off. It is also readily saponified by concentrated sulphuric acid in the cold. All attempts to remove the two hydrogen atoms of the dihydro-benzene derivative were fruitless.

It was now of interest to know whether this same product can be obtained from benzyl chloride and disodic succino-succinic ether.

β -, γ -, and π -Dihydro-dibenzyl-dioxyterephthalic ether,



Disodic succino-succinic ether contains, dried in a desiccator, 20 per cent. of alcohol, which is detrimental for all reactions and must therefore be removed. This is possible in part by heating for half an hour at 100° or until 15 per cent. of the alcohol is driven off. It is impossible to drive off the remaining 5 per cent. of alcohol, since, as soon as this is accomplished, the salt burns up spontaneously. At first several portions were lost in this way. The sodium salt therefore, containing about 5 per cent. of alcohol, was used in all reactions carried out with this salt.

On treating the salt with benzyl chloride, reaction takes place only on heating to the boiling point of the benzyl chloride; with benzyl iodide, however, reaction takes place at 100° . In both cases identical products are obtained, and the preparation and purification is exactly the same as with benzyl-dioxy-terephthalic ether (*q. v.*). There is formed a colorless product insoluble in alkalis, which crystallises from alcohol in needles melting at 128° . This was at first regarded as a perfectly homogeneous substance, entirely different from the two isomeric β - and γ -derivatives obtained from it and described below. Dr. W. Muthmann, however, proved by an optical investigation that the above product, melting at 128° , is only a mixture of β -dihydro-dibenzyl-dioxy-terephthalic ether (melting point 148.5°) and of γ -dihydro-dibenzyl-dioxy-terephthalic ether (melting point 140.5°), which two substances furthermore are remarkably alike in appearance. The mixture of the two isomers shows naturally a lower melting point than either of the constituents. It was thereupon found possible to separate the isomers, since the β -isomer is less soluble in alcohol. By repeated recrystallisation from much alcohol, whereby only the crystals first separating out were collected, the β -isomer was obtained pure and perfectly homogeneous, and melting at 148.5° .

This substance was first obtained from the above mixture by violent sublimation, whereby the lower melting γ -isomer is decomposed by preference.

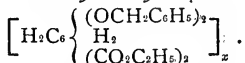
0.1289 gram substance dried at 110° gave 0.3353 gram CO_2 and 0.0770 gram H_2O .

	Theory for $\text{H}_2\text{C}_6 \left\{ \begin{array}{l} (\text{OCH}_2\text{C}_6\text{H}_5)_2 \\ \text{H}_2 \\ (\text{CO}_2\text{C}_2\text{H}_5)_2 \end{array} \right.$	Found.
C	71.56	71.03
H	6.42	6.67

The substance treated for a long time in alcoholic solution with zinc dust and hydrochloric acid is not further reduced, and is in great part recovered unchanged. Phenylhydrazine and hydroxylamine do not react on it. It is also not possible to remove the two hydrogen atoms in the dihydro-benzene derivative by oxidation: nitrogen trioxide passed in large excess into a chloroform or alcoholic solution of the substance leaves it unchanged. Similar negative results were obtained with chromic acid in acetic acid solution. Bromine in carbon bisulphide solution, which so readily converts the corresponding benzoyl and acetyl ethers into benzene derivatives, causes in this case an evolution of hydrobromic acid, but very likely bromine is substituted for hydrogen in the benzyl groups; products containing bromine, insoluble in alkalis, and having a low melting point, are obtained.

The optical study of the β -isomer by Dr. Muthmann gave the following results: "Fine needles, isolated, with no tendency to collect together in aggregates. The total reflection is sharp and parallel to the elongated direction of a crystal. A pinacoid plane predominates, through which the acute bisectrix comes out perpendicularly. The axial angle is much larger than in the case of the γ -isomer: the axes are yet visible at the edges of the field of vision. A characteristic difference between the two isomers lies in the fact that while in the γ -isomer (melting point 140.5°) the axial plane is parallel to the elongation of the crystal, in the case of the β -isomer (melting point 148.5°), the axial plane lies perpendicular to the elongation of the crystal."

π -Dihydro-dibenzyl-dioxyterephthalic ether,



By dissolving the β -isomer just described in concentrated sul-

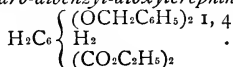
phuric acid in the cold, it is converted into a polymer which crystallises finely. For its preparation, however, it is better to take the above-mentioned mixture of β - and γ -isomers, melting at 128° , whereby the γ -isomer, which is not affected, can also be obtained pure. This is dissolved in concentrated sulphuric acid, and after standing in the cold for about ten minutes, poured into water, extracted with chloroform, washed with alkalies, etc. There remains after distilling off the chloroform a mixture of about 75 per cent. γ -isomer and 25 per cent. polymer. Since only traces of the polymer dissolve in boiling alcohol, while the γ -isomer is very soluble therein, a separation is readily possible. The polymer was treated repeatedly with hot alcohol, and finally recrystallised from acetic acid, from which solvent it was obtained in large colorless, measurable crystals, which often look like octahedra or dodecahedra.

0.1840 gram substance, dried at 140° , gave 0.4795 gram CO_2 and 0.1060 gram H_2O .

	Theory for $\left[\text{H}_2\text{C}_6 \left\{ \begin{array}{c} (\text{OCH}_2\text{C}_6\text{H}_5)_2 \\ \text{H}_2 \\ (\text{CO}_2\text{C}_2\text{H}_5)_2 \end{array} \right\} \right]_x \cdot$	Found.
C	71.56	71.08
H	6.42	6.40

The substance melts at 272° and is volatile without change, but at a much higher temperature than the α -, β - and γ -isomers, whereby, as well as because of the difficult solubility in all solvents except hot acetic acid, the fact that the substance is a polymer is unquestionable.

γ -Dihydro-dibenzyl-dioxyterephthalic ether,



This substance is formed together with the β -isomer by treating disodic succino-succinic ether with benzyl chloride or iodide. The alcoholic mother-liquors, from which the β -isomer has been removed, contain the γ -isomer, but it is very difficult to obtain the latter free from β -isomer, by fractional crystallisation from alcohol. The solutions, from which the β -isomer has been in part removed, are therefore evaporated, and then dissolved in concentrated sulphuric acid. Or the above mixture of β - and γ -isomers, melting at 128° , obtained directly from disodic succino-succinic ether, is

dissolved in concentrated sulphuric acid. The β -isomer is thus polymerised, while the γ -isomer remains unchanged. Since hot alcohol readily takes up the γ -isomer, whereas the polymer dissolves only in traces, a separation is now accomplished with ease. From the alcoholic solution on concentration the γ -isomer is obtained in long, lustreless needles, grouped together in sheaves, and melting at 140.5° .

0.2121 gram substance, dried at 110° , gave .05538 gram CO_2 and 0.1270 gram H_2O .

	Theory for $\text{H}_2\text{C}_6 \begin{Bmatrix} (\text{OCH}_2\text{C}_6\text{H}_5)_2 \\ \text{H}_2 \\ (\text{CO}_2\text{C}_2\text{H}_5)_2 \end{Bmatrix}$	Found.
C	71.56	71.21
H	6.42	6.65

The substance is volatile without decomposition; it does not react with phenylhydrazine or hydroxylamine, nor is it changed by long reduction with zinc dust and hydrochloric acid in alcoholic solution. In its behavior towards nitrogen trioxide, chromic acid and acetic acid, and also towards bromine, it is entirely analogous to the β -isomer (*q. v.*).

The optical results of Dr. Muthmann are as follows: "Needles, which have a great tendency to collect in fibrous asbestos-like aggregates. Isolated crystals have predominating a plane through which an acute bisectrix comes out perpendicularly. The axial angle is very small, at most 5° , so that the crystals, like isotropic bodies, remain dark in parallel light with crossed Nicols. The axial plane is parallel to the elongation of the crystal, and is exactly perpendicular to the predominating plane."

On treatment of disodic succino-succinic ether with benzyl chloride or iodide, two isomeric compounds are formed, both of which show the behavior of alkylated phenol ethers. The fact that the β -isomer polymerises so easily is a proof that it contains doubly bound carbon atoms.

The fact that the so-called α -dihydro-dibenzoyl-dioxy-terephthalic ether obtained by reduction of dibenzyl-dioxy-terephthalic ether, is not identical with either of the products obtained from succino-succinic ether, is not surprising, since six isomeric dihydro-benzene derivatives are possible (see introduction).

The study of the acid ethers of dioxyterephthalic ether and of succino-succinic ether has led to results which are even more conclusive, if that is possible, than those obtained with the alkyl ethers.

10 grams disodic dioxy-terephthalic ether gave with acetyl chloride, 7 grams (calculated 9 grams) of pure diacetyl derivative, melting at 154° , and identical with the product obtained by Wedel.¹ This substance is not acted upon by an excess of bromine, even after long standing in chloroform solution. It is split into its constituents by sulphuric acid in the cold.

10 grams disodic succino-succinic ether gave with acetyl chloride 2.5 grams (calculated 11 grams) diacetyl derivative, melting at 169° , and identical with Wedel's product.¹ It is very unstable, and even by recrystallisation from alcohol it is slowly decomposed into acetic ether and succinylo-succinic ether: it is insoluble in alkalis. Bromine converts it in chloroform solution into dioxy-terephthalic ether (cf. page 404), with evolution of hydrobromic acid. These results are entirely in accordance with those obtained in the pyromellithic acid series. Remarkable, however, to a high degree is the fact that diacetyl-dioxy-terephthalic ether and diacetyl-succino-succinic ether form crystals from acetic ether, which show not the slightest difference by a most careful inspection, and even the goniometrical results show a most remarkable resemblance. Were it not for the difference in melting point (15°), and total difference in chemical behavior towards bromine, the substances might be regarded as identical.

The following results were kindly given me by Dr. W. Muthmann:

"Diacetyl-dioxy-terephthalic ether, melting point 154° , monoclinic system.

$$a : b : c = 1.9292 : 1 : 1.2037, \beta = 71^{\circ} 1'.$$

Diacetyl-succino-succinic ether, melting point 169° , monoclinic system.

$$a : b : c = 1.9814 : 1 : 1.2225, \beta = 69^{\circ} 39\frac{1}{2}'.$$

Planes the same for both: $m = (110) = \infty P$; $c = (001) = oP$; $\rho = (\bar{1}01) = +P\infty$; $\omega = (\bar{1}11) = +P$.

The fundamental angles are as follows:

	Diacetyl-dioxy-tereph. Ether.	Diacetyl-succino-succ. Ether.
$m : m$	$122^{\circ} 32'$	$123^{\circ} 25'$
$m : c$	$81^{\circ} 0'$	$80^{\circ} 31'$
$c : \rho$	$63^{\circ} 17'$	$63^{\circ} 44'$

Thereby the complete isomorphism of the two substances is proven."

¹Ann. Chem. (Liebig) **219**, 81, 85.

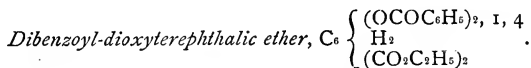
These facts show how much some dihydro-benzene compounds resemble in physical respects the corresponding benzene derivatives. They are isomorphous, and can therefore form isomorphous mixtures with one another.

A similar observation has been made by Dr. Muthmann in the study of the dihydro-terephthalic acids of v. Baeyer,¹ and his results have been published in Groth's *Zeitschrift für Krystallographie*, Band 17, p. 460.

Furthermore, also benzoyl dioxy-terephthalic ether (melting point 174°) and α -benzoyl-succino-succinic ether (melting point 165°) show a like remarkable resemblance one to the other, and also form isomorphous mixtures with one another.

The fact that diacetyl and α -dibenzoyl-succino-succinic ether are dihydro-benzene derivatives is unquestionably proved by what follows.

In view of the isomorphism existing between the above-mentioned benzene and dihydro-benzene derivatives, the fact that succino-succinic ether itself, which is now to be regarded as a dihydro-dioxy-terephthalic ether (Δ 1, 4 or Δ 2, 5), forms isomorphous mixtures² with dioxy-terephthalic ether and other hydroxylated benzene derivatives is no longer surprising.



Benzoyl chloride acts instantly on disodic dioxyterephthalic ether, but in order to make the benzoyl derivative it is better simply to dissolve dioxyterephthalic ether in sodium hydroxide and to shake with benzoyl chloride.³ In this way 20 grams were converted quantitatively into the benzoyl derivative, which re-crystallised once from alcohol is pure.

0.2150 gram substance, dried at 110°, gave 0.5272 gram CO₂ and 0.0966 gram H₂O.

	Theory for C ₆ $\left\{ \begin{array}{l} (OCOC_6H_5)_2 \\ H_2 \\ (CO_2C_2H_5)_2 \end{array} \right.$	Found.
C	67.53	66.88
H	4.76	4.98

The substance is difficultly soluble, even in boiling alcohol

¹Ann. Chem. (Liebig) 251, 285.

²O. Lehmann, *Zeitschr. für phys. Chemie* 1, 16.

³Udransky and Baumann, *Ber. d. chem. Ges.* 21, 2744.

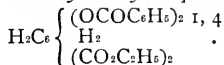
(about seven grams dissolve in a liter), and crystallises therefrom in long colorless needles, melting at 174° . The solutions are colorless, and show no fluorescence or coloration with ferric chloride. The substance volatilises without decomposition, and is not affected in the least on long standing in chloroform solution with bromine. Concentrated sulphuric acid splits it into benzoic acid and dioxyterephthalic ether, while two molecules of sodium ethylate in alcoholic solution decompose it into benzoic ether and disodic dioxyterephthalic ether.

Exactly as in the case of dibenzoyl-dioxy-pyromellithic ether, the benzoyl groups are stable in alcoholic solution towards hydrochloric acid, so that it is possible by reduction to obtain hydrogenated benzene derivatives. In this way in all five isomeric dihydro-dibenzoyl-dioxy-terephthalic ethers were obtained which show an entirely analogous behavior.

Reduction with Aqueous Hydrochloric Acid.—Five grams dibenzoyl-dioxy-terephthalic ether were very finely pulverised and dissolved in as little boiling alcohol as possible (about 750 cc.), and then much zinc dust and concentrated hydrochloric acid added, in order to produce a very violent evolution of hydrogen. After about 15 minutes the reduction is complete, since repeated treatment of the reduction products thus obtained for 15 minutes longer did not show the slightest difference in the composition of the reduced products. The alcoholic solution is now poured into a large amount of water, and then extracted with chloroform and washed with sodium hydroxide, etc. Thus always about 2.5 grams of reduction-product were obtained, which proved to be a mixture of three isomeric dihydro-dibenzoyl-dioxy-terephthalic ethers, and the separation of these could be accomplished very sharply.

Since one of the three isomers thus obtained is also formed directly from disodic succino-succinic ether, it will be advantageous to describe its preparation here.

a-Dihydro-dibenzoyl-dioxy-terephthalic ether,



Disodic succino succinic ether reacts even at ordinary temperature with benzoyl chloride, and the reaction is completed by

gentle heat on a water-bath. After treatment with chloroform, sodium hydroxide, etc., 4.5 grams pure dibenzoyl derivative are obtained from 10 grams of the salt. It crystallises from alcohol in long colorless needles, melting at 165° , which show a remarkable resemblance to dibenzoyl-dioxy-terephthalic ether, and forms isomorphous mixtures with it. The first named substance is, however, much more easily soluble in hot alcohol.

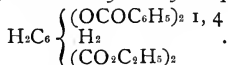
0.2118 gram substance, dried at 110° , gave 0.5205 gram CO_2 and 0.1007 gram H_2O .

	Theory for $\text{H}_2\text{C}_6 \left\{ \begin{array}{l} (\text{OCOC}_6\text{H}_5)_2 \\ \text{H}_2 \\ (\text{CO}_2\text{C}_2\text{H}_5)_2 \end{array} \right.$	Found.
C	67.24	67.02
H	5.17	5.28

The substance remains unchanged when treated for 15 minutes in alcoholic solution with zinc dust and concentrated hydrochloric acid, and from 0.5 gram substance taken, 0.3 gram pure substance, melting at 165° , was recovered. It is volatile without decomposition. Concentrated sulphuric acid splits it in the cold into benzoic acid and succino-succinic ether. The succino-succinic ether contains in this case always traces of dioxyterephthalic ether, which forms isomorphous mixtures with it. The same observation was made in splitting diacetyl-succino-succinic ether (melting point 169°) with concentrated sulphuric acid (cf. page 416). In both cases, therefore, a slight oxidation takes place on saponification.

The α -dibenzoyl-derivative remains unchanged on treatment with an excess of nitrogen trioxide in alcoholic or chloroform solution. Chromic acid in acetic acid solution completely destroys one portion, while much unchanged substance is recovered. It is, however, possible to remove the two hydrogen atoms by treating the substance in dilute carbon bisulphide solution with exactly the calculated amount of bromine (2 atoms). There is formed quantitatively, with evolution of hydrobromic acid, dibenzoyl-dioxy-terephthalic ether, melting at 174° , and on saponifying it with concentrated sulphuric acid pure dioxyterephthalic ether melting at 133° was obtained.

β - and γ -Dihydro-dibenzoyl-dioxy-terephthalic ether,



The above mixture of α -, β -, and γ -dihydro-dibenzoyl-dioxy-

terephthalic ethers can be separated as follows: 3 grams are dissolved in about 150 cc. alcohol, and subjected to fractional crystallisation. The least soluble fractions give finally (in very small quantity in comparison to the other two isomers present) a substance, crystallising in needles, which, by repeated recrystallisation, shows the constant melting point 165° , and in its entire behavior is identical with the above-described α -dihydro-dibenzoyl-derivative obtained from succino-succinic ether. The fractions more soluble in alcohol show the presence of two isomers, the one crystallising in spheres composed of an aggregation of needles, the other, in long, flat needles. The difference in solubility is very slight; sometimes crystals separate from a saturated solution, which consist entirely of one form only, but this is a matter of chance. Finally the following method of separation was found to be exceedingly sharp. The mixture of β - and γ -isomers is dissolved in as little warm ether as possible, and then a small amount of petroleum ether (boiling point 33° – 50°), wherein the products are insoluble, added. On cooling, or standing in a flask without disturbance, transparent cubes, rectangular plates, and long, flat needles which have the ends cut off obliquely and are often grown into one another, separate out. These can be separated mechanically with ease, and often once crystallised, and thus separated were perfectly pure. It is generally necessary, however, to recrystallise the portions separated mechanically from ether with addition of a little petroleum ether, and again separate mechanically the portions that crystallise out. The concentrated ethereal filtrates give new crops of crystals again; it is important to see to it that a complete evaporation of the mother-liquor over the crystals never takes place. In this way the above transparent cubes, constituting what has been named the β -isomer, are obtained with a sharp melting point 138° : they remain unchanged by sublimation or repeated recrystallisation or by treatment in alcoholic solution with reducing agents, zinc dust and hydrochloric acid. The β -isomer is dimorphous, crystallising not only in cubes, but also in rectangular plates (mentioned above), which, however, represent the less stable modification.

0.1464 gram substance, dried at 110° , gave 0.3596 gram CO_2 and 0.0698 gram H_2O .

	Theory for $\text{H}_2\text{C}_6\left\{\begin{array}{l} (\text{OCOC}_6\text{H}_5)_2 \\ \text{H}_2 \\ (\text{CO}_2\text{C}_2\text{H}_5)_2 \end{array}\right.$	Found.
C	67.24	66.99
H	5.17	5.29

The substance crystallises from ether or carbon disulphide in cubes or in long, rectangular plates. The latter represent the less stable modification, and heated, they undergo at 110° a change, becoming turbid and melting on higher heat sharply at 138° , just as the cubes. From alcohol the β -isomer was generally obtained in small spheres consisting of needles, owing to the fact that the substance separates out at first in oil globules. Once it was obtained in long, glistening needles.

For the following account of the optical properties of the substance I am indebted to the kindness of Dr. Muthmann. "*Cubes* :—Perfectly transparent crystals. 1 plane with diagonal extinction; 2 plane with parallel extinction. Through the first plane a bisectrix, but no axes, appears. Recrystallised from carbon disulphide on an object-glass, the cubes give a mixture of cubes and of rectangular plates (the latter predominating).

"*Rectangular plates* :—An acute bisectrix comes out almost perpendicularly through the principal plane. The axial angle is not very large; the double refraction medium. Both axes readily seen. The plane of the optic axis is perpendicular to the elongation of the crystal."

The β -isomer is converted, on treatment with concentrated sulphuric acid in the cold, into benzoic acid (melting point 120°) and succino-succinic ether (melting point 127°). On dissolving in much carbon disulphide and treating with the calculated amount of bromine (2 atoms), it is converted quantitatively into dibenzoyldioxy-terephthalic ether (melting point 174°) with evolution of hydrobromic acid.

The above-mentioned long flat needles, having the ends cut off obliquely, remain unchanged by repeated recrystallisation, and melt sharply at $102\frac{1}{2}^{\circ}$. The analysis and behavior prove that these constitute a third isomer, namely, γ -dihydro-dibenzoyldioxy-terephthalic ether.

0.1353 gram substance, dried at 110° , gave 0.3313 gram CO_2 and 0.0642 gram H_2O .

	Theory for $\text{H}_2\text{C}_6 \left\{ \begin{array}{l} (\text{OCOC}_6\text{H}_5)_2 \\ \text{H}_2 \\ (\text{CO}_2\text{C}_2\text{H}_5)_2 \end{array} \right.$	Found.
C	67.24	66.78
H	5.17	5.27

The substance is volatile without change; reducing agents do not reduce it further. In its behavior towards sulphuric acid and

bromine it is entirely analogous to the β -isomer (*g. v.*). It is soluble with ease in all organic solvents except petroleum ether.

Dr. Muthmann reports the following optical properties: "Large transparent crystals. The angle of extinction found to be 14° – 18° . No axis or bisectrix is seen through the predominant plane. The angle which the end planes make with the elongation of the crystal was found to vary in different specimens."

Reduction of Dibenzoyl-dioxy-terephthalic Ether with Alcoholic Hydrochloric Acid and Zinc Dust.

Remarkably enough, the reduction of dibenzoyl-dioxy-terephthalic ether goes in an entirely different way by using an alcoholic instead of aqueous solution of hydrochloric acid. For the reduction, alcohol saturated at 15° with hydrochloric acid was used; otherwise the method is the same as that followed above with aqueous hydrochloric acid. Fifteen minutes' reduction is sufficient, as a much longer treatment does not cause the slightest change in the composition of the reduction products, and only lowers the yield. After pouring into an excess of water, extracting with chloroform, washing with caustic alkalies, etc., there is left about 2.5 grams of reduction-product (from 5 grams substance taken). This consists of a mixture of three, probably four, isomeric dihydro-dibenzoyl-dioxy-terephthalic ethers. One of these isomers can readily be separated from the others by fractional crystallisation from alcohol or ether. The first difficultly soluble fractions yield finally, by repeated recrystallisation, a substance crystallising in needles and melting at 165° . It is identical in every respect with the above-described α -dihydro-dibenzoyl-dioxy-terephthalic ether, and is formed here in much greater amount than by the reduction with aqueous hydrochloric acid. The isomers, more readily soluble in alcohol and ether, were repeatedly fractionated from ether with addition of a little petroleum ether. Although often large transparent measurable crystals were obtained which could be separated mechanically, and these again subjected to fractional crystallisation, it was found impossible to accomplish a sharp separation of the isomers, or to obtain single crystals which gave a sharp melting point. It was possible, however, to settle with certainty that two isomers were at hand which show a great tendency to form isomorphous mix-

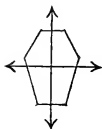
tures, as well with one another as with α -dihydro-dibenzoyl-dioxy-terephthalic ether, wherefore it is not likely that a separation can ever be accomplished. In this way crystals were obtained melting from 85° – 95° , and crystallising in long transparent rectangular plates. These often have the ends cut off obliquely in a very peculiar way and are not regularly developed. Then also crystals were observed melting between 100° – 110° , and forming acute rhombic plates. The fractions most soluble in ether and petroleum ether melt at 75° – 78° , and consist probably of a third isomer; but since it always separates out as an oil at first, no definite-shaped crystals can be obtained.

An optical investigation of the above crystals by Dr. W. Muthmann has proved with certainty that two distinct isomers are at hand, and that these are totally different from the above-described α , β , and γ -isomers. He reports thereon as follows:

1. "Transparent crystals, melting point 85° – 95° ; the above *rectangular plates*. The axial plane is perpendicular to the elongation of the crystal. Through plane 1 an optical axis comes out almost perpendicularly, the bisectrix is yet visible at the edge of the field of vision; system probably monoclinic, planes 2 and 3 prismatic, 1 and 4 ortho."



2. "The above *rhombic plates*, melting point 100° – 110° . Very complete extinction noticeable, great resemblance to diacetyl-succino-succinic ether."



Although a separation of the isomers was not possible, still the above proves with certainty that at least three, and perhaps four, isomers are formed by reduction with alcoholic hydrochloric acid. That they are all dihydro-dibenzoyl-dioxy-terephthalic ethers is proved by the fact that on saponification with concentrated sulphuric acid, pure benzoic acid (melting point 120°) and pure succino-succinic ether is formed from all.

The above experiments prove conclusively that the ethers of succino-succinic ether and of dioxy-terephthalic ether have the substituted group bound to oxygen, and furthermore the behavior of the isomeric dihydro-dibenzoyl-dioxy-terephthalic ethers makes it exceedingly probable that succino-succinic ether itself is nothing but a dihydro-dioxy-terephthalic ether. That this substance ever appears as a ketone, or that it is necessary in order to explain its reactions to assume a pseudo-ketone formula, is in the present

state of our knowledge of this compound without the slightest experimental proof.

Finally, there is appended a brief description of a series of compounds which completes the work on durene.¹

Methyl dinitro-pyromellithate, made from the silver salt with methyl iodide. Transparent long flat needles, melting at 180.6° (from methyl alcohol). Analysis:

	Found.	Theory.
C	41.90 per cent.	42. per cent.
N	7.36	7.
H	3.33	3.

Methyl diamido-pyromellithate, obtained by reduction of the nitro derivative with zinc dust and acetic acid. Long flat needles (from methyl alcohol), melting at 149.6°, and possessing the color of potassium bichromate. Oxidising agents convert it not into the diimide,² but into a stable red azo-derivative very difficultly soluble in all solvents except hot acetic acid. Analysis:

	Found.	Theory.
C	49.40 per cent.	49.41 per cent.
H	4.94	4.71

Methyl p-diketo-hexamethylene-tetracarboxylate, or as it must now be called *methyl dihydro-dioxy-pyromellithate*, obtained by reduction of the amido compound with zinc dust and sulphuric acid. Colorless, strongly refractive cubes (from benzene) possessing a high specific gravity and a melting point 175°. The solutions show a faint blue fluorescence and give with ferric chloride a deep red coloration. Soluble in caustic, not in mild alkalis. Analysis:

	Found.	Theory.
C	48.82 per cent.	48.84 per cent.
H	4.92	4.65

Methyl dioxy-pyromellithate, obtained from the diketo compound with bromine. Granular yellow powder (from methyl alcohol) showing a green fluorescence and melting at 207°. Volatile without decomposition, but does not form good crystals. Analysis:

¹ Annalen der Chemie 237, 1.

² This Journal 11, 5.

	Found.	Theory.
C	48.72 per cent.	49.12 per cent.
H	4.39	4.09

Methyl quinone-pyromellithate, obtained from the hydroquinone or from methyl diamido-pyromellithate by oxidation with nitric acid. Crystallises from methyl alcohol in *colorless needles*, which contain two molecules methyl alcohol.

	Theory for $C_6\{CO_2CH_3\}_4 + 2CH_4O.$	Found.
C	47.52	47.37
H	4.95	5.32

Heated to 150° it loses the crystal alcohol and changes to a pure yellow color. It then sublimes in yellow needles and melts at 208°. Analysis:

	Found.	Theory.
C	49.19 per cent.	49.41 per cent.
H	3.90	3.53

In these experiments, which were in part carried out in the chemical laboratory of Purdue University, La Fayette, Indiana, I have been most zealously assisted by Dr. V. Paepcke. It is a pleasure to me to have this opportunity of expressing to him my warmest thanks.

WORCESTER, MASS., May 2, 1890.

ON THE EFFECT OF TEMPERATURE UPON THE DETERMINATION OF AMMONIA BY NESSLERISATION.

BY ALLEN HAZEN AND HARRY W. CLARK.

In making a number of distillations of standard ammonium chloride solution to determine the loss due to incomplete condensation, as stated by Dr. Smart,¹ results were obtained similar to those given by him, namely, that only from 85 to 95 per cent. of the ammonia taken was found in the distillate. It was observed,

¹ Report of the National Board of Health, 1882; also this Journal 11, 367.

however, that no more ammonia was obtained when the end of the condenser dipped below the surface of cold water, and also that by repeatedly redistilling a distillate from standard ammonium chloride solution, no more was lost than by a single distillation. The loss could not therefore be due to incomplete condensation.

The cause of this apparent loss was found to be the low temperature of the distillates. The city water, at a temperature of 5° , running about the block-tin condensers, cooled the distillate to nearly the same temperature, and the time that the tubes stood before nesslerising was insufficient to warm them to the temperature of the room. It was found that the color obtained by nesslerising an ammonia solution depends upon its temperature. The warmer the solution the deeper will be the color produced, so that a standard containing 4 cc. of ammonia solution nesslerised at 30° will give a color equal to that obtained from 5 cc. nesslerised at 15° , or 6 cc. nesslerised at 0° . A change in temperature after nesslerising will not change the color very much.

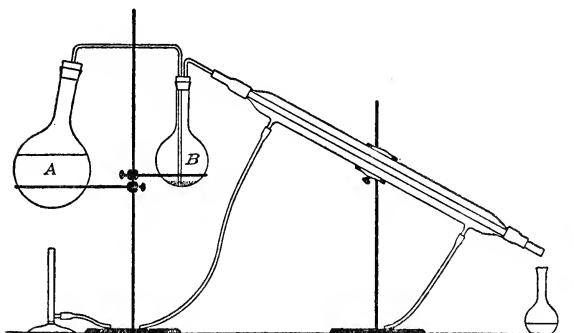
To obtain accurate results it is necessary to bring standards and distillates to the same temperature before nesslerising. This is easily accomplished by allowing them to stand in a room with even temperature for a sufficient time. It was found that the difference between the temperatures of two 50 cc. nessler tubes of water, standing side by side, was reduced to one-half every thirteen minutes. With racks of three dozen tubes each, the adjustment was much slower, forty-five minutes being required to reduce a difference of 10° to 5° . When the possible difference in temperature between different tubes at the start is 10° or more, three or four hours will be required to bring them to a sufficiently even temperature. We find it most convenient to let them stand over night. Standards and distillates are made ready for nesslerisation during the day, and all stand on the same table over night. In the morning they are nesslerised and compared. There is not the slightest loss by evaporation of ammonia in this way, even upon standing some days, and in a laboratory where ammonia fumes are excluded there is no danger of absorption of ammonia from the air.

Our earlier conclusion, that there is no loss of ammonia by incomplete condensation, has been confirmed by numerous determinations made in this way, with most satisfactory results. The condenser tubes used are of block tin, twenty inches long and three-eighths inch internal diameter.

APPARATUS FOR THE DETERMINATION OF AMMONIAS IN SAND AND SEWAGE.

BY ALLEN HAZEN.

In examining sand from filters it has been thought desirable to determine free and albuminoid ammonia, as this shows the amount of organic matter stored, in the same terms as it is given for the filtered water or sewage.



To accomplish this, the apparatus shown by the figure has been used during the last two years. A liter flask, *A*, filled with ammonia-free water, serves simply to supply steam. A small glass tube carries the steam to the bottom of the small flask *B*, which contains the sand. The steam passing through the sand very rapidly removes all free ammonia. Alkaline permanganate solution is then put in *B* and the distillation continued. The albuminoid ammonia is given off much more rapidly than in the ordinary water distillation, owing to the concentration of the permanganate which is put upon the sand full strength, while in water-analysis it is diluted to eight or ten times its volume by the water. One portion of 50 cc. invariably contains all the free ammonia. The first portion of albuminoid ammonia, when boiling rapidly, usually contains at least eight or nine tenths of the whole, and the second portion has almost all of the rest, so that only two tubes need be collected. Bumping is impossible. The condensa-

tion of steam in the small flask is not excessive, but if necessary it may be heated with a low flame.

I have found this apparatus to be well adapted to the examination of sewage and anything which contains enough ammonia. The great bulk of a pure water which it would be necessary to use prevents its application to ordinary water-analysis.

The amount of free ammonia thus obtained is the same as that found by the usual process of dilution with pure water and direct distillation. The albuminoid ammonia is commonly a little greater, owing to the concentration of the permanganate, but the results are sharper and different determinations agree with each other more closely. There is also a very considerable saving of time when a number of determinations are to be made.

I prefer to use rubber stoppers and connections. It requires considerable boiling to get new rubber entirely free from ammonia, but once free there is no more trouble, and a stopper will last for a very long time.

LAWRENCE EXPERIMENT STATION, MASS. STATE BOARD OF HEALTH.

ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH AND LEE K. FRANKEL.

In this, our third communication¹ upon the above subject, we have the following to offer. By reference to an article entitled "The Electrolytic Method applied to Palladium,"² it will be noticed that it was there stated that the deposition of this metal from the solution of its double cyanide was not possible so long as any undecomposed potassium cyanide remained in the solution. Acting upon this observation, we have attempted the separation of the palladium from the metals which are deposited from their double cyanide solutions, with what success the results appended will show.

Mercury from Palladium.

Solutions of mercuric chloride and of palladium chloride were used in these experiments, potassium cyanide being added, so

¹ This Journal 12, 104; and Proceedings of Chem. Section of Frank. Inst., Vol. I, p. 119.

² This Journal 12, 212.

that the precipitate first formed is completely dissolved. In the results recorded below the potassium cyanide is, as a rule, in large excess, so that there is no danger of the current precipitating any cyanides from the solution.

	Mercury present, in grams.	Palladium present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Mercury found.	Difference in percent- age from theoretical.
(1)	0.0886	100 %	3	200 cc.	.08 cc.	.0891	+0.56 %
(2)	"	"	"	"	"	0.0886	...
(3)	"	"	"	"	0.1	0.0886	...
(4)	.2215	"	"	"	0.22	0.2220	+0.22
(5)	"	"	"	"	"	0.2205	-0.45
(6)	"	"	"	"	"	0.2234	+0.85
(7)	"	"	"	"	"	0.2231	+0.72
(8)	.2266	"	"	"	0.20	0.2267	+0.04
(9)	"	"	"	"	"	0.2266	...
(10)	"	"	"	"	"	0.2251	-0.66
(11)	"	"	"	"	"	0.2260	-0.26

The above figures indicate that the separation is satisfactory. In all of the experiments the current was allowed to act for sixteen hours.

Silver and cadmium being metals which, like mercury, separate quite easily and readily from cyanide solutions when acted upon by a feeble current, we naturally expected that their separation from palladium would be unattended by any particular difficulty. In this we were sadly disappointed, for out of a series of ten experiments made with varying quantities of alkaline cyanide, and with currents varying in strength from 0.5 cc. to 0.1 cc. oxyhydrogen gas per minute, we failed to obtain either silver or cadmium free from the palladium. The presence of these two metals, in fact, appeared to favor the deposition of the palladium from the solution.¹

Mercury from Arsenic.

Our investigations with arsenic showed us that the metal could not be deposited from solutions of the alkaline arsenites or arseniates, nor from solutions containing alkaline cyanides. In the separation of mercury from arsenic, the precipitate formed on adding a solution of mercuric chloride to a solution either of potassium arsenite or arseniate was dissolved in potassium cyanide and subjected to the action of the current. The separation proceeds without any difficulty.

¹ This Journal 12, 213.

	Mercury present, in grams.	Arsenic present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Mercury found.	Difference in percent- age from theoretical.
(12)	0.2266	100 %	3	200 cc.	0.3 cc.	0.2277	+0.48 %
(13)	"	"	"	"	"	0.2251	-0.66
(14)	"	"	"	"	"	0.2266	...
(15)	"	"	"	"	"	0.2259	-0.30
(16)	"	"	"	"	"	0.2274	+0.35

Time of deposition was sixteen hours.

Cadmium from Arsenic.

In this instance we discovered that the separation was not complete unless the arsenic existed in the solution as the higher oxide. Experiments conducted with arsenious compounds gave a deposit of cadmium which was invariably dotted over its surface with black spots of metallic arsenic. With the arsenic present as arseniate of potassium, and with the solution for electrolysis prepared as under the separation of mercury from arsenic, the appended results were obtained.

	Cadmium present, in grams.	Arsenic present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas. per minute.	Cadmium found.	Difference in percent- age from theoretical.
(17)	0.2124	100%	3	200 cc.	0.1 cc.	0.2110	-0.65%
(18)	"	"	2.2	"	"	0.2104	-0.93
(19)	"	"	"	"	0.35	0.2128	+0.19
(20)	"	"	"	"	"	0.2113	-0.52
(21)	"	"	1.5	"	0.4	0.2123	-0.05
(22)	"	"	"	"	"	0.2120	-0.19
(23)	"	"	"	"	0.8	0.2123	-0.05
(24)	"	"	"	"	0.6	0.2118	-0.28
(25)	"	"	"	"	0.8	0.2120	-0.19
(26)	"	"	"	"	0.6	0.2116	-0.37

Silver from Arsenic.

The conditions essential for thorough deposition are the same here as those mentioned under the separation of cadmium from arsenic. Attempts to separate the two metals from solutions in which the arsenic existed as lower oxide resulted in the deposition of the arsenic with the silver. Using arseniate solutions, however, the results are satisfactory, as shown below.

	Silver present, in grams.	Arsenic present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Silver found.	Difference in percent- age from theoretical.
(27)	0.1572	100%	2.2	200 cc.	0.15 cc.	0.1577	+0.31%
(28)	"	"	1.5	"	"	0.1572	...
(29)	"	"	2.2	"	0.3	0.1572	...
(30)	"	"	"	"	"	0.1577	+0.31
(31)	"	"	1.5	"	0.35	0.1579	+0.44
(32)	"	"	"	"	"	0.1567	-0.31
(33)	"	"	"	"	"	0.1582	+0.63
(34)	"	"	"	"	"	0.1573	+0.06

The time required for the precipitation of the metal was the same as that required for those which precede this and for those which follow, viz. sixteen hours.

Copper from Arsenic.

All that has been said concerning the separation of silver from arsenic will apply equally as well here, the only point of difference being the increased strength of current necessary for the deposition of the copper. Thrown out from such a solution, the copper appears as a firm, compact and lustrous coating; it can be readily washed and shows no tendency to oxidise. The results obtained are as follows:

	Copper present, in grams.	Arsenic present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Copper found.	Difference in percentage from theoretical.
(35)	0.1772	100%	3	200 cc.	1.5 cc.	0.1765	-0.39%
(36)	"	"	...	"	5	0.1778	+0.33
(37)	"	"	...	"	10	0.1766	-0.33
(38)	"	"	...	"	5	0.1762	-0.56

The potassium cyanide should be carefully added until the precipitate formed dissolves and the solution assumes a pink tinge. An excess of potassium cyanide is not harmful, but the greater the excess the longer will be the time required for the deposition, since the current will not deposit the copper until this excess is decomposed.

We have also attempted the separation of copper from arsenic in a solution containing an excess of ammonia.¹ The results obtained were satisfactory, but the method is one requiring skill for its successful performance and close attention to details in order to insure accurate results. From such a solution the copper is deposited as a spongy coating, and, like all such coatings, has a tendency to carry down and retain the salts of the alkalies which are in the solution. Our results are as follows:

	Copper present, in grams.	Arsenic present.	NH ₄ OH.	Total dilution.	Current strength in cc. OH gas per minute.	Copper found.
(39)	0.1772	100%	Large excess.	200 cc.	1.3 cc.	0.1797
(40)	"	"	"	"	0.7	0.1754
(41)	"	"	3 cc.	"	1.1	0.1783

¹ See McCay, *Chemiker Zeitung* 14, 509.

While experimenting with the oxides of tungsten and molybdenum we found that they dissolved readily in potassium cyanide, and that in such solutions, or in solutions of ammonium tungstate and ammonium molybdate in the presence of potassium cyanide, no deposition of either metal occurred, even under the influence of strong currents. With this knowledge the following separations were effected.

Mercury from Tungsten.

For this separation, weighed quantities of mercuric chloride and ammonium tungstate were dissolved in water, the precipitate of tungstate of mercury dissolved in potassium cyanide, and the resulting solution subjected to the action of the current.

	Mercury present, in grams.	Tungsten present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Mercury found.	Difference in percent- age from theoretical.
(42)	0.2266	100%	2.2	200 cc.	0.7 cc.	0.2282	+0.70%
(43)	"	"	3	"	0.8	0.2282	+0.70
(44)	"	"	2.2	"	"	0.2268	+0.09
(45)	"	"	1.5	"	0.7	0.2281	+0.66
(46)	"	"	1.5	"	"	0.2280	+0.61

By employing solutions of ammonium tungstate, mercuric chloride and potassium cyanide, in the amounts indicated above, the deposition of the mercury will follow without carrying down with it any tungsten as oxide. It was noticed that when the current strength exceeded that given in the experiments, a slight coating of oxide of tungsten made its appearance on the mercury, although it seemed to be fully removed during the process of washing. The slightly higher results found in the table are not, however, due to this cause. Tungsten was not found in these deposits, though careful search was made for it.

Silver from Tungsten.

The conditions essential for this separation are the same as those in the preceding.

	Silver present, in grams.	Tungsten present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Silver found.	Difference in percent- age from theoretical.
(47)	0.1572	100 %	1.5	200 cc.	0.7 cc.	0.1566	-0.38 %
(48)	"	"	"	"	"	0.1580	+0.50
(49)	"	"	1	"	"	0.1579	+0.44
(50)	"	"	"	"	"	0.1587	+0.95
(51)	"	"	"	"	"	0.1579	+0.44
(52)	"	"	.75	"	"	0.1583	+0.70

Cadmium from Tungsten.

In this separation, the condition of extreme importance is the strength of current. It was found that if the current used was stronger than that mentioned in the following table, the deposits were apt to become spongy and the results correspondingly high.

	Cadmium present, in grams.	Tungsten present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Cadmium found.	Difference in percentage from theoretical.
(53)	0.2408	100 %	2.2	200 cc.	0.6 cc.	0.2422	+0.58 %
(54)	"	"	1.5	"	"	0.2396	-0.49
(55)	"	"	"	"	"	0.2408	...
(56)	"	"	"	"	"	0.2425	+0.70
(57)	"	"	"	"	"	0.2411	+0.12
(58)	"	"	"	"	"	0.2409	+0.04

Mercury from Molybdenum.

The method utilised here was the same as the one found effective in the separation from tungsten. The precipitate obtained on adding mercuric chloride to the solution of ammonium molybdate was dissolved in potassium cyanide and then exposed to the action of the current. The results found and the conditions necessary are indicated in the table.

	Mercury present, in grams.	Molybdenum present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Mercury found.	Difference in percentage from theoretical.
(59)	0.2266	100 %	1.5	200 cc.	1 cc.	0.2271	+0.22 %
(60)	"	"	2.2	"	"	0.2283	+0.79
(61)	"	"	3	"	"	0.2273	+0.30
(62)	"	"	2.2	"	"	0.2272	+0.26
(63)	"	"	3	"	"	0.2275	+0.35

Silver from Molybdenum.

The silver was added in the form of nitrate, the conditions otherwise being similar to those under the separation of mercury from molybdenum.

	Silver present, in grams.	Molybdenum present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Silver found.	Difference in percentage from theoretical.
(64)	0.1572	100 %	1.5	200 cc.	0.8 cc.	0.1576	+0.25 %
(65)	"	"	2.2	"	0.8	0.1580	+0.50
(66)	"	"	3	"	0.4	0.1583	+0.70
(67)	"	"	1.5	"	"	0.1573	+0.06
(68)	"	"	2.2	"	"	0.1578	+0.38

Cadmium from Molybdenum.

In these separations, the tendency of the cadmium to form spongy deposits was not so noticeable. In most cases the coating was dense and compact, and hence permitted thorough washing.

	Cadmium present, in grams.	Molybdenum present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Cadmium found.	Difference in percentage from theoretical.
(69)	0.2408	100 %	2.2	200 cc.	0.4 cc.	0.2392	—0.66 %
(70)	"	"	1.5	"	"	0.2431	+0.91
(71)	"	"	"	"	"	0.2416	+0.33
(72)	"	"	2.2	"	"	0.2410	+0.08
(73)	"	"	3	"	"	0.2400	—0.33

Copper from Bismuth.

So far as we are aware, there has not as yet been a successful method proposed for the electrolytic separation of these two metals. Knowing that bismuth¹ could be completely deposited from solutions of the citrate containing excess of alkali, we added to such a solution copper sulphate and then a slight excess of potassium cyanide, and found that under such conditions the bismuth was deposited without carrying down with it any of the copper. Having convinced ourselves that this was true, we instituted the following separations, which prove the accuracy of the method. It is necessary for complete deposition that sufficient citrate and alkali be present to keep the solution clear upon the addition of the potassium cyanide.

	Bismuth present, in grams.	Copper present.	Citric acid present, in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Bismuth found.	Difference in percentage from theoretical.
(74)	0.0946	...	3	200 cc.	1 cc.	.0952	+0.63 %
(75)	"	...	"	"	"	.0940	—0.63
(76)	"	...	"	"	"	.0948	+0.21
(77)	"	100 %	"	"	"	.0949	+0.31
(78)	"	"	"	"	"	.0941	—0.51
(79)	"	"	"	"	"	.0947	+0.10
(80)	"	"	"	"	"	.0947	+0.10
(81)	"	"	"	"	"	.0947	+0.10

While these figures indicate a complete separation, we would advise careful compliance with the conditions of the experiment, otherwise the results will prove to be discordant. The deposit

¹ This Journal 5, 114.

often occurs spongy and is apt to loosen from the dish on washing, so that great care is necessary at this point.

In all of the separations mentioned above we washed the deposited metal with boiling water, except in the case of bismuth, where washing with cold water and absolute alcohol proved decidedly advantageous. The drying was done upon a moderately warm iron plate. The current used in all cases was derived from Daniell cells of the crowfoot pattern.

UNIVERSITY OF PENNSYLVANIA, April 30, 1890.

Contributions from the Laboratory of Purdue University.

III.—UPON THE CARBOHYDRATES OF PEACH GUM.

BY W. E. STONE.

A certain class of vegetable products known as "gums" or "mucous" or mucilage yield as the result of hydrolytic action, glucose-like bodies. These, whenever carefully studied, have, almost without exception, been identified as either *galactose* or *arabinose*. When heated with a dilute solution of sulphuric acid, gum arabic yields sometimes galactose and sometimes arabinose,¹ although it is not quite clear whether this is a specific characteristic of a distinct gum, or whether there may not be gums of different origins sold under the one name. The gum exuding from the bark of the cherry tree produces by hydrolytic action, *arabinose*.² Tragacanth gum yields the same product.³ The mucilage occurring in the seed-coats of linseed, quince seeds, etc., yields also glucoses, which, however, have not been satisfactorily isolated or identified. A gum-like substance which can be extracted from lignified tissues by alkalis yields by hydrolysis, *xylose*.⁴ A gum exudes from the bark of the peach tree (*Persica vulgaris*) following injury, or from the fruit of the same when punctured by insects, which, with one exception, has not been

¹ Claesson, Ber. d. chem. Gesell. **14**, 1270.

² Claesson, Sachsse u. Martin, Phytochemische Untersuchung, 69.

³ Sandersleben, Ibid.

⁴ Koch, Pharmaceutische Zeitschrift für Russland **25**. Also Wheeler and Tollens, Ber. d. chem. Gesell. **22**, 1046.

studied. The wild peach tree, escaped from cultivation in the middle southern United States, produces this gum in considerable quantities, and from this source I obtained 200–300 grams, in air-dried weight, of gum as collected from the bark, and a somewhat less quantity from the fruit. The former was of a dark brown color and contained many impurities, such as bits of bark, leaves, etc.; that from the fruit exuded in clear drops, which soon hardened on exposure to the air to transparent or semi-opaque tears, and was of course of a higher grade of purity than that from the bark.

This gum was soluble in water, by which it first became swollen to a marked degree, and in solution showed a slightly acid reaction, and a distinct, although not strong, laevo-rotation.

After my investigation had been in progress some time I learned of R. W. Bauer's results obtained from peach gum which was probably of European origin. By treating the same with a dilute solution of sulphuric acid he secured a crystalline sugar-like substance which possessed the specific rotation $(\alpha)_D = 76.02^\circ$, and which he regarded as identical with galactose, although lack of material had evidently prevented confirmatory tests. From this he concluded that the peach gum contained the carbohydrate from which galactose is derived by hydrolysis. A preliminary examination of the gum in my possession indicated, however, that it also contained the substance from which arabinose is derived, as well as that mentioned by Bauer, and this was confirmed by further investigation.

The two portions of gum were examined separately, although all stages of the examination showed them to be of practically the same nature. As preliminary to a close study, portions of both gums were subjected to the furfurol test for the presence of an arabinose-producing substance,¹ and to the mucic acid test for a similar source of galactose.²

By distillation at 125° – 130° C. with sulphuric acid kept at a constant density of 1.254, concentration of the distillate, and precipitation with dilute ammonia, the following data were obtained:

Gum from bark:—2.5 grams yielded .1181 gram of furfuralamide, or 4.72 per cent.

Gum from fruit:—2.5 grams yielded .1214 gram of furfuralamide, or 4.84 per cent.

¹ Stone and Tollens, *Ann. Chem. (Liebig)* **249**, 227.

² Kent and Tollens, *Ann. Chem. (Liebig)* **227**, 228.

By oxidation with nitric acid of 1.15 specific gravity, mucic acid was produced as follows:

Gum from bark:—5 grams yielded .618 gram of mucic acid, or 12.36 per cent.

Gum from fruit:—2.5 grams yielded .423 gram of mucic acid, or 16.92 per cent.

These results indicated the presence in the gum of those substances which yield *arabinose* and *galactose* upon hydrolysis, and the course of the investigation was directed toward isolating and identifying the same. 110 grams of the gum from the bark of the peach tree were dissolved in 880 cc. of dilute sulphuric acid of 1.03 specific gravity, and the solution heated on the water-bath for ten hours. At the end of this time the liquid was of a dark amber color, much humin-like substance had been separated, and the vapors gave an intense red color upon paper moistened with aniline acetate, indicating the formation of furfural. The liquid was neutralised with barium carbonate, filtered and evaporated, yielding a thick dark-colored sirup which reduced Fehling's solution strongly. In the same way 50 grams of the gum from the peach fruit were dissolved in 400 cc. of dilute sulphuric acid of 1.03 specific gravity, and heated during nine hours with the same results as in the previous case.

The dark-colored impure sirups thus obtained were boiled with strong alcohol for about an hour, whereby a dark gummy substance was precipitated. From this the clear alcoholic solution was decanted and again evaporated, after which crystallisation soon followed. In this way 21.3 grams of a white crystalline product were obtained from the bark gum, or nearly 20 per cent. of the material taken. From the fruit gum a proportionally smaller quantity was obtained. Both products were sweet, and reduced Fehling's solution strongly. After recrystallisation, the specific rotations of each were determined as follows:

From bark gum:—3 grams in a solution of 30 cc. showed an average dextro-rotation of 19.16° or $(\alpha)_D = 98.4^\circ$.

From fruit gum:—3 grams in a solution of 30 cc. showed an average dextro-rotation of 19.04° or $(\alpha)_D = 95.2^\circ$.

These numbers indicated the identity of the two products, but did not correspond to the specific rotations of any of the known glucoses or sugar-like bodies, although that of the product from bark gum approximated the specific rotation of arabinose. They

differed also decidedly from Bauer's result ($(\alpha)_D = 76.02^\circ$). A mixture of two substances like arabinose and galactose, however, would give a polarising number like that obtained. Moreover, the preliminary tests for mucic acid and furfural had indicated the formation of both of these compounds. The next step, therefore, was an attempt to separate these products by means of fractional crystallisation into their constituents. By crystallisation from absolute alcohol each of the two original products was separated into several portions, the specific rotations of which showed a curious relation to that of the original substance.

From the sugar from bark gum, which showed the specific rotation of 98.4° , five fractions were obtained, which, in the order of their separation, showed the following polarising numbers:

I. $(\alpha)_D = 97.5$	IV. $(\alpha)_D = 94.3$
II. " $= 73.5$	V. " $= 96.3$
III. " $= 93.0$	

The sugar from fruit gum, which had the specific rotation 95.2 , was separated into two portions, which gave the following polarising numbers:

I. $(\alpha)_D = 75.0$	II. $(\alpha)_D = 94.8$
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In both cases it is to be noted that a fraction was separated with a much lower specific rotation than the original without increasing the specific rotation of the other fractions. These fractions ultimately included all of the mother-liquor; hence it may not be assumed that a higher polarising sugar remained in solution. In the sugar from fruit gum it is certainly remarkable that the original portion polarising 95.2° should have been resolved into one polarising 75.0° and another polarising at 94.8° , which latter number is practically the same as the original. There was no marked disproportion in the quantity of the fractions. The separations were made from alcohol at the ordinary laboratory temperature, which conditions could scarcely affect or change the specific rotations of the bodies in solution.

Of the fractions from the sugar from bark gum, numbers I, II and III, while not agreeing exactly with the polarisation constants for arabinose and galactose, still approached them. They were therefore recrystallised and gave respectively the following numbers:

Ia, $(\alpha)_D = 98.8^\circ$
IIa, " $= 82.09^\circ$
IIIa, " $= 98.9^\circ$

In like manner also the fractions from the sugar of the fruit gum were recrystallised. I. was unfortunately lost by an accident, but its specific rotation, as already observed (75.0°), leaves little doubt that it would also have given a result similar to that of II. of the bark-gum product. II. showed after recrystallisation the specific rotation 101.6° .

Nos. Ia and IIIa of the product from the bark gum were again recrystallised and yielded a product with the specific rotation $(a)_D = 102.3^\circ$. As results, therefore, of these repeated and tedious fractional separations, there were obtained, from the bark gum, two products: one with the specific rotation 102.3° , which approximated very closely that of arabinose (104°), and a second with the specific rotation 82.09° , which is practically that of galactose. From the fruit gum also we obtained two products which were undoubtedly identical with those from the bark gum, and which according to their specific rotations were also respectively arabinose and galactose.

These comparatively pure products were now subjected to some confirmatory tests in order to leave no doubt as to their nature.

Arabinose being a pentaglucose, $C_5H_{10}O_5$, has in common with xylose, the only other known member of the class, the characteristic reaction of producing furfural in large quantities when distilled with sulphuric acid.¹ Xylose, however, has the specific rotation $(a)_D = 18^\circ - 19^\circ$,² and was therefore quite out of the question in connection with the body already described with the specific rotation 102.3° . 0.9246 gram of the latter was distilled with sulphuric acid of 1.254 specific gravity (the loss by distillation being replaced by a regular constant addition of water to the distilling flask), until the distillate no longer gave a distinct coloration on paper moistened with aniline acetate. The distillate being then concentrated by fractional distillation and treated with dilute ammonia gave a precipitate of furfuramide, which on being dried weighed 0.1843 gram, or 19.93 per cent. of the weight of sugar taken. This result taken with the specific rotation leaves no doubt as to the identity of this product with arabinose. From a very small quantity a phenylhydrazine compound was prepared, which was, however, insufficient for recrystallisation, and, in the impure state, showed the melting point of 145° .

¹ Loc. cit.

² Wheeler and Tollens, Ber. d. chem. Gesell. **23**, 1046.

A well known specific reaction for galactose is the formation of mucic acid when subjected to the action of nitric acid. The other portion of sugar from bark gum, polarising at 82.09° , was heated on a water-bath with nitric acid of 1.15 specific gravity. 0.5025 gram received 20 cc. of nitric acid, and the whole was heated until two-thirds of the original volume was evaporated. 0.288 gram of mucic acid was thus produced, or 57.3 per cent. of the weight of sugar taken. A phenylhydrazine compound was also formed which melted at 154° . These reactions, coupled with the specific rotation, identifies the second product as galactose.

The gummy substance secreted from the tissues of the peach tree, as above described, contains, therefore, those bodies which by hydrolysis yield arabinose and galactose. The occurrence of these bodies together under these circumstances is the more noteworthy from the fact that arabinose and galactose represent two distinct classes of carbohydrates, the true glucoses and the pentaglucofoses, and are not usually found in such intimate connection with each other. The gum arabic is, I believe, the only other instance where such occurrence has been recognised, and in no previous case has the isolation and recognition of both these carbohydrates from a single homogeneous substance been accomplished.

LA FAYETTE, IND., *May*, 1890.

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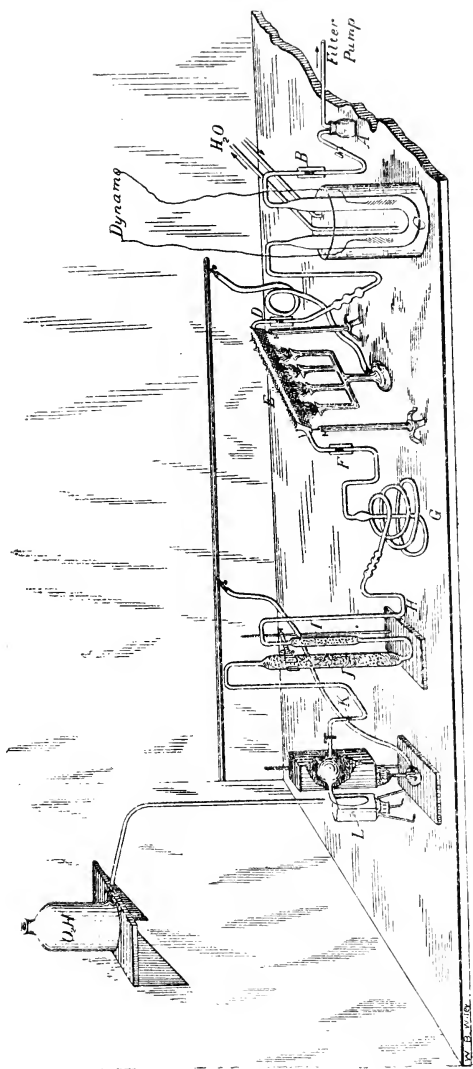
THE ATOMIC WEIGHT OF OXYGEN.

BY W. A. NOYES.

II.

At the conclusion of my first paper¹ the opinion was expressed that the determinations there reported were affected by some source of constant error which had not been discovered. A careful study of all sources of error which I can think of, or which others have been able to suggest, has compelled me, now, to adopt a different conclusion. In view of the further determinations to be described in this paper, and in view of all the experiments which have been tried for the purpose of detecting sources of error, it does not seem to me possible that the *experimental results* of that first series can be in error by more than one part in a thousand. An error in the principle of calculation employed has, however, been detected. In applying the correction for the water obtained by re-oxidising the reduced copper, only *eight-ninths* of the weight of this water was added to the weight of oxygen found. The *total* weight of this water should have been added, since, if all the water could be removed at once, the oxygen found would be greater by the weight of this water and not simply by the weight of the oxygen which it contains. When correctly calculated, the result of this series becomes 15.896. The result of the four series which are now completed does not differ from this by so much as one part in thirty thousand.

¹ This Journal 11, 155.



The hydrogen used in these further determinations has been obtained by the electrolysis of dilute sulphuric acid containing from fifteen to twenty per cent. of the pure acid. The arrangement of the apparatus employed is apparent from the accompanying cut. The voltameter at first used was made for me by Bender and Hobein of Munich. When this was broken by accident, a new one was made by myself. The platinum electrodes were six centimeters by two, and were soldered with gold solder to wire one millimeter in diameter. The solder on the oxygen side was corroded away after a time and the wire was then threaded through the electrode. The distance between the electrodes around the bend of the tube was twelve to fifteen centimeters, and the height of the tube about thirty centimeters. The dynamo used gave a potential of from fifty to sixty volts, and this gave from three to four liters of hydrogen an hour. The current was regulated by a coil of platinum wire immersed in water. By changing the point of contact with this coil the rate of evolution could be instantly changed between quite wide limits and, in this way, suited to the rate of absorption in the copper oxide apparatus. In case of too rapid absorption, the drawing of the acid over into the purifying apparatus could be prevented by attaching a Bunsen pump to the bottle through which the oxygen passed. This was rarely used. In most of the determinations, after connection was once established with the copper oxide apparatus, the hydrogen was passed in continuously, under normal atmospheric pressure, until that part of the experiment was complete.

About 140 cc. of the dilute sulphuric acid were used at first, and when the volume became too small, freshly boiled water was introduced through the tube on the oxygen side. This could be done, of course, without allowing any air to enter the apparatus.

The only impurities which hydrogen generated in such an apparatus can contain are oxygen, ozone, hydrogen dioxide, water, compounds of sulphur, and traces of nitrogen. The first three were removed by passing over heated copper or heated platinised asbestos. The former was used for the determinations of the second series and of the first half of the third series. For the remaining determinations platinised asbestos was used. There seems to be a slight tendency to lower results in these last determinations, but it does not exceed 0.005 H, and I doubt very much if it has any significance. The platinised asbestos would, in the

presence of hydrogen, convert all compounds of sulphur into hydrogen sulphide. The hot copper seems to have the same effect; at least, traces of hydrogen sulphide were apparent from the formation of lead sulphide in the purifying apparatus which followed. The amount of lead sulphide formed was very minute, apparently not exceeding a few milligrams for more than a hundred liters of hydrogen.

Following the asbestos tube is an absorption apparatus containing a solution of fifty parts water, twenty parts caustic potash and two parts of lead sulphate. This was placed in a spiral tube made of tubing of about seven millimeters internal diameter and about four meters in length. The amount of the impurity to be removed from the gas is very small, hence it is a large surface of liquid, rather than a large amount, which should be exposed to its action. Ten or fifteen cc. of the solution is sufficient to keep the walls of such a tube as is described thoroughly moistened, while the capacity of the tube is about 150 cc. At the rate of four liters an hour, any given portion of the gas will take two minutes in passing through it. Dr. C. L. Mees has kindly estimated for me the average number of contacts of the molecules of hydrogen with the walls of a tube of this size in this length of time. He finds that, on the average, each molecule would strike the walls of the tube 600 times in two minutes. The calculation was based on the coefficient of diffusion of hydrogen into itself and on the coefficient of viscosity.

After passing the spiral tube the gas next passed over a few sticks of caustic potash which gradually dissolved in the water brought over from the solution. Next it passed over stick potash and then over phosphorus pentoxide, or, in the third series, over sodium wire.

The joints at the ends of the tube of hard glass containing the copper or the platinised asbestos, were made of rubber tubing covered on the outside with water. On the oxygen side, the connection with a tube dipping under mercury was made in the same way. All other joints were made by sealing the glass. Under an external pressure corresponding to several inches of mercury, the apparatus stood for several weeks without any evidence of leakage. But the best evidence that no leakage occurred is found in the results of the determinations recorded below. In the last series *only 2 cc. of nitrogen were obtained from over sixty liters of hydrogen.*

The apparatus used for the oxidation of the hydrogen has been essentially the same as that described in my first paper. The apparatus has been simplified by bending the side tube for collecting the water downward, instead of making a T connection as in the former apparatus. The apparatus is opened at the end of this tube to introduce the copper oxide and to remove the reduced copper, and, by determining the volume of this tube up to a certain mark, the redetermination of the volume of the apparatus after each experiment becomes unnecessary. For most of the determinations described in this paper the apparatus was blown and the attachment to the stopcock was made by myself. The glass commonly used for "sealing tubes" was employed. The temperature used in my apparatus, as determined somewhat roughly by an air-thermometer, has been about 450° . At this temperature the slightest change in the shape or volume of the bulb was never observed. I was misled by a dealer into the statement that the apparatus used in my first determinations was made of hard glass. Such was not the case.

The connection with the hydrogen apparatus was made by a ground glass joint. After bringing the parts together, the grease in the joint was melted and allowed to solidify. The connection was not again interfered with till the entrance of the hydrogen was complete. This method of connection seems to give almost absolute surety against leakage.

A question of the greatest importance in these determinations is as to how closely the weight of the apparatus can be relied on after heating it for several hours. This was twice carefully tested by heating the vacuous apparatus for three or four hours under the same conditions as those of a determination. After rinsing and wiping the apparatus, there was at first an apparent loss of between one and two milligrams. The next morning the weight was in one case two-tenths, in the other three-tenths of a milligram less than before the heating. A correction of this amount would lower the final value for the atomic weight by about 0.005 H, but I do not feel justified in applying any such correction, and I doubt very much if the error from this source is always in the same direction. In the three series of determinations described in this paper, the weights whose difference gave the weight of the hydrogen were always determined in the morning without opening the balance case, and after the apparatus had

hung on the balance over night. The counterpoise remained on the balance from the beginning to the end of each determination. It is believed that, with the small apparatus which has been used, more is gained by securing constancy in the condition of the apparatus than by attempting to vary the conditions of the apparatus and of the counterpoise in the same way. The volume of the apparatus used has varied from about 80 to 100 cc., and the weight from 130 to 150 grams.

In resuming the work, an attempt was made at first to find some substance which could be used in place of the copper oxide. It was hoped that some substance could be found from which the hydrogen and the water could be expelled without the necessity of a re-oxidation. Lead chromate was at first tried and gave a value of about 15.10. The reduced chromate retained considerable amounts of water which could not be expelled at the temperature used.

Manganese dioxide was next tried. In the first experiment this was heated to dull redness in a copper crucible for some time. This gave the value 16.64. The substance had retained water, both before and after the experiment. A second determination, with manganese dioxide which had been ignited over the blast, gave 15.83. Considerable water was found in the reduced oxide. Later, another determination was made with the ignited oxide, and after expelling the water as far as possible and weighing the apparatus, the reduced oxide was emptied into a combustion tube and the residual water was driven over into a phosphorus pentoxide tube. This gave the value 15.968. Another specimen of the oxide of equal amount, after ignition and heating in the exhausted apparatus in exactly the same manner as in the first part of this last experiment, retained 14 mg. of water which could be driven out by heating in a combustion tube. If a correction of this amount is applied, the value becomes 15.904. I consider this result as of some interest as indicating that my results are not affected to any notable extent by the copper oxide employed. A better guarantee, however, is given by the conduct of the copper oxide itself as described below.

Litharge was also tried, but its action is slow, and in the attempt to hasten it by raising the temperature, using a triple burner, the bulb collapsed.

Returning to the copper oxide, the following method of pro-

cedure was adopted. After expelling the water, as described in my first paper, the heating of the vacuous apparatus was continued for half an hour, the connection with the bulb surrounded with ice being retained. The apparatus was then closed, cooled, and weighed. Dry air was then allowed to enter, the end of the side tube was opened and the copper oxide and reduced copper were transferred quickly to a combustion tube. The latter was always ignited in a current of dry air shortly before use. The copper oxide and metallic copper were then ignited in a current of oxygen, and the water obtained was collected in a phosphorus pentoxide tube. The oxygen was, of course, displaced by dry air before weighing, and a counterpoise of similar volume was used in determining the weights. The correction for the water obtained is much smaller than in the first series, and in the second series it is only one part in a thousand. The smallness of the correction is in part due to a more complete expulsion of the water.

It might be objected that the copper oxide would absorb water in its transference to the combustion tube. This took but a few seconds, but the matter was made the subject of a direct test. The apparatus was filled with copper oxide, heated and exhausted in the usual way. Dry air was then admitted and the copper oxide was transferred to the combustion tube and ignited. Seven-tenths of a milligram of water was obtained. This includes, also, any error which would arise from the retention of water by the copper oxide at the beginning of the experiment. This would correspond to less than 0.002 H in the value of the atomic weight and would tend to raise it.

G. Stillingfleet Johnson¹ has called my attention to the fact that reduced copper retains *water*. I can confirm his statement, but I cannot acknowledge that any considerable error was introduced in my first series from this source. I have carefully read his paper and I find nothing to show that *re-oxidised* copper retains water. On the contrary, he shows that ignition in nitrogen,² even, will expel all the water and hydrogen retained by the copper.

To test the retention of water by the reduced copper, the following experiment was tried. After the removal of the water in a determination carried thus far in the usual way, a small amount of dry air was admitted and the apparatus was again weighed. It was then heated and exhausted and the nitrogen obtained was

¹ Chem. News 59, 272.

² J. Chem. Soc. 1879, 242.

measured. The apparatus, also, was cooled and weighed. The loss in weight, less the weight of nitrogen found, gave the weight of the water removed from the apparatus. This was found to be 3.2 mg. It would seem that this must have been nearly or quite all present as *water*, and that it was dislodged from the pores of the reduced copper by heating in the atmosphere of nitrogen. The reduced copper and the copper oxide were then transferred to a combustion tube and the hydrogen and water determined by ignition in a current of oxygen. 1.8 mg. of water was obtained in this way. There were at least 18 to 20 grams of reduced copper in this experiment. When such a weight of copper retains only 0.2 mg. of hydrogen in any form which it will give up at a bright red heat in a current of oxygen, I think no one will claim that, after such ignition, any amount which can affect the determinations can still remain.

Mr. Johnson thinks, also, that the presence of sulphur in my copper oxide may have introduced an error in my work. I find by careful tests an exceedingly minute trace of sulphur, it is true, but I am unable to see how this can affect the results. It is evident that in the removal of the main portion of the water no sulphur can escape. The only chance for error lies then in the amount of water obtained by the re-oxidation of the copper. But this water could be seen to condense in the front part of the tube and afterwards to evaporate at a temperature below the boiling point of water. It is evident, therefore, that it contained no appreciable amount of sulphuric acid. Sulphur dioxide would pass through the phosphorus pentoxide tube unchanged. A further guarantee of the substantial accuracy of the determination of this residual hydrogen and water is the small effect of the correction involved. In the last three series this correction affects the result by about 0.02 H, or about the same as the correction to vacuum in the experiments of Cooke and Richards, or of Keiser, and nearly ten times less than the correction to vacuum by the method of Dumas.

A careful consideration of all sources of error which I can see leads me to believe that there can be no constant error affecting the determination of the weight of the oxygen by more than one or two milligrams, and I think the absolute error is rarely, if ever, greater than that. An error of one milligram affects the result by about 0.002 H.

The question of the trustworthiness of my result resolves itself, then, into a question of the purity of my hydrogen and the accuracy of the determination of its weight. The accuracy of weighing is evident from the agreement among themselves of the determinations of the last two series, taken in connection with the fact that the *conditions of each pair of weighings were as nearly as possible identical*. This last factor is of the greatest importance. By determining the weight before the entrance of the hydrogen with an apparatus which had stood over night, and then determining the weight after the entrance of the hydrogen with an apparatus which had been cooled for several hours, but which had been recently rinsed and wiped, results quite accordant among themselves could be obtained, but the results might be higher than the truth by 0.02 to 0.04 H.

I have sought in every direction which I could think of or which my friends could suggest for evidence of impurities in my hydrogen, but, in every case but one, without success.

Nitrogen was always present, but the amount is very small, and any uncertainty in the amount of the correction to be applied must be entirely insignificant in its effect. It is perhaps conceivable, though very improbable, that ammonia or oxides of nitrogen might be formed. The water obtained was tested with Nessler's reagent with a negative result. The test for nitrous acid with sulphanilic acid and naphthylamine gave in the first case a slight color. A second trial, with greater care to exclude the air, gave no result. Oxides of nitrogen, if formed, might be retained by copper oxide at 450°. Accordingly the copper oxide and reduced copper from one experiment were placed in a combustion tube, which was then connected with the Sprengel pump and exhausted while cold. The mixture was then heated to bright redness for an hour. 0.02 mg. of nitrogen was obtained. In this experiment 0.7 mg. of carbon dioxide was also obtained. Whether this came from a little organic matter or from a trace of calcium carbonate in the copper oxide I cannot say. I do not consider it as practically significant.

Professor Morley has called my attention to the fact that copper oxide sometimes gives off gases slowly when heated in a vacuum. To test this point, the apparatus was filled with copper oxide and the air pumped out as usual. After standing for twenty-four hours it was heated again for four hours and the gases given off

were pumped out and measured. They consisted of 0.039 mg. of carbon dioxide and 0.035 mg. of nitrogen. It seems evident that no error of practical importance arises from this source.

To test for sulphur dioxide, which might pass through the purifying apparatus,¹ ten liters of the hydrogen were passed through a Geissler potash bulb containing a solution of potassium permanganate having one-tenth milligram of available oxygen. The solution retained its color, paling slightly. The loss of color was equally rapid by merely standing in an atmosphere of hydrogen. The solution in the spiral tube of the purifying apparatus, after the passage of 100 liters of hydrogen, showed, when acidified with sulphuric acid, the presence of only an exceedingly minute trace of any substance which would reduce a permanganate solution. The conversion of the sulphur compounds into hydrogen sulphide seems to be, therefore, practically complete.

Professor Morley has suggested to me that carbon in some form might be present in the hydrogen. About nine liters of hydrogen were passed over copper oxide heated in a combustion furnace, and the water formed was condensed in lime water. The latter remained perfectly clear. The water obtained in the determinations was repeatedly tested for carbon dioxide by adding baryta water, and always with negative results. A trace of carbon dioxide was sometimes found in the nitrogen, but only in one case did it exceed one-tenth cc. In that case it was about 0.24 cc. and probably came from the copper oxide, which was from a different source and probably less pure than that used in all the other determinations. In this experiment (the fourth of the last series), the carbon dioxide was left out of the calculation entirely, as it would be without appreciable effect on the weight of the oxygen.

A test for oxygen was made by passing ten liters of hydrogen through a solution of chromous chloride as suggested by v. Pfordten.² The result was negative. I do not, however, place much reliance on this test, but am rather disposed to rely on the impossibility that oxygen can pass heated copper, especially in an atmosphere of hydrogen. A more satisfactory test for oxygen would probably be to condense a considerable amount of the hydrogen in palladium and afterwards expel it, causing it to pass through a weighed phosphorus pentoxide tube. Unfortunately I have not been able to apply this test.

¹ Cooke and Richards, this Journal **10**, 98.

² Ann. Chem. (Liebig) **228**, 121.

Cooke¹ has recently shown that the efficiency of a phosphorus pentoxide tube may become seriously impaired by use. In the last series more than 100 liters of hydrogen passed through my purifying apparatus, and it was thought wise to test this point, especially as the amount of the drying agent was somewhat less than usual, owing to the difficulty of preparing the sublimed pentoxide which was used. A U-tube with glass stoppers and having the glass tube on one side bent downward and drawn out to fit the socket of my hydrogen apparatus, was filled with phosphorus pentoxide. After passing hydrogen through the tube to displace the air it was closed, noting temperature and pressure, and weighed. A counterpoise of the same size and shape was used. 72 liters of hydrogen were then passed through the tube and it was again weighed. There was absolutely no increase in weight. A decrease of about one-tenth mg. was partly accounted for by change of temperature and pressure. The efficiency of the drying tube is probably due in part to the fact that the gas was almost completely dried by stick potash before it came to the pentoxide tube.

The results of the third and fourth series show that it is possible by my method to distinguish between two specimens of hydrogen, one of which contains less than one-tenth mg. of water per liter, while the other is dry so far as it is possible to say that any gas is dry.

As an illustration, I give here the record in my note-book of one of the determinations of the fourth series.

Volume of apparatus, . . . 79.73 cc.

“ “ tare, . . . 77.35

“ “ weights, . . . 1.83

Tare at 8 A. M. Friday = 15.3335. $t^{\circ} = 19^{\circ}.8$, Bar. = 754.

Hydrogen was passed into the apparatus for $2\frac{1}{4}$ hours.

Tare at 12 M. Friday = 16.1033

“ 2 P. M. “ = 16.1042

“ 8 A. M. Saturday = 16.1042. $t^{\circ} = 23^{\circ}.6$, Bar. = 748.

Gain = 0.7707.

The water and gas were expelled.

Tare at 11 A. M. Saturday = 9.2237

“ 1 P. M. “ = 9.2246.

Loss = 6.1089.

¹ This Journal 11, 522.

The gas obtained was measured as follows :

$$\begin{array}{ll}
 V = 1.9 = 0.615 \text{ cc.} & \text{Log. } \frac{0.001256}{(1 + 0.00367t)760} = 6.18012 \\
 t^{\circ} = 25^{\circ} & \\
 \text{Bar.} = 748.2 & \text{Log. } 0.615 = 1.78888 \\
 b = 421. & \text{" } 302.4 = 2.48058 \\
 T = 23.5 & \text{Log. of weight of } N = 4.44958 \\
 B' = 303.7 - 1.3 = 302.4 & N = 0.00028.
 \end{array}$$

After treating with caustic soda the nitrogen remaining was 0.00024.

$$\begin{array}{r}
 1.3149 \\
 1.3005 \\
 \hline
 \text{Water by re-oxidation} = 0.0144
 \end{array}$$

$$\text{At. W.} = \frac{6.1233 \times 2}{0.7704} = 15.896.$$

I give, next, the more important details of each series, including statements with regard to rejected experiments.

First Series.

This is the series the results of which were published in my first paper. But little need be added to the statements there given. The hydrogen was generated from zinc and hydrochloric acid. Nine experiments in this series were lost or rejected. Three of these were strictly preliminary and precautions afterwards used were omitted. Two were carried no further than the weighing of the hydrogen. In one a little mercury got into the tube through which the hydrogen passed. In one the amount of hydrogen was small, less than two-tenths of a gram, and in one air got into the hydrogen generator. In one sulphuric acid instead of hydrochloric was used to generate the hydrogen. When properly calculated, this last determination becomes 15.890 instead of 15.874, as given in my first paper. (See page 441.)

Second Series.

In this and the succeeding series the hydrogen was obtained by electrolysis as already described. The results of this series are far more discordant than those of any of the other series and contain both the highest and lowest results of all the series. I am not able to give a satisfactory reason for this.

In the first four determinations of the series the hydrogen was dried by a tube filled with phosphorus pentoxide and asbestos,

which had been used for some time. Fearing that this drying tube might have lost its efficiency, it was replaced by a new tube filled with phosphorus pentoxide and having a capacity of about 200 cc. The last two results of the series were obtained with hydrogen dried by this tube and are the lowest of the series, except the fourth, which falls between them. In preparing the sublimed phosphorus pentoxide used in the fourth series it was found that the pentoxide used contained some substance, probably the trioxide, which took fire and burned when heated in a current of oxygen. The presence of a small amount of the trioxide in the large amount of the pentoxide used *may* have caused the low results of these two determinations. I did not feel justified in rejecting them, however, and no determination of any series has been rejected because it gave a high or low result.

Eleven experiments in this series were lost or rejected. In eight of these other substances than copper oxide were used and the results have been described. One was carried only through the weighing of the hydrogen. One was lost by a leakage of the stopcock, and one was made with hydrogen dried by recently distilled sulphuric acid. This last gave the value 15.877.

Third Series.

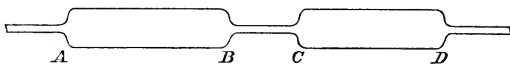
The results of the last two determinations of the second series led me to fear that my hydrogen was contaminated by something coming from the phosphorus pentoxide employed. I determined, therefore, to use a different drying agent and to avoid the use of the pentoxide altogether. A volume of 140 cc. in a large tube was closely packed with sodium wire.

The wire was one half millimeter in diameter and about 20 grams of it were used. This tube was then substituted for the pentoxide tube, the rest of the purifying apparatus remaining essentially unchanged. With hydrogen dried in this way the results of the third series were obtained. Four experiments in this series were lost, three of them by a leakage at some point in the work, and the fourth by reason of a drop of mercury which by some accident got into the side tube and was not discovered till the experiment was nearly completed. The hydrogen was tested by burning from a platinum jet and gave not the faintest sodium color. Indeed, it was with extreme difficulty that the flame could be seen at all in daylight. It was the hydrogen from this apparatus which was tested for carbon with negative results.

The hydrogen from the apparatus was not, however, free from water. Thirty-five to forty liters of the hydrogen were passed through a phosphorus pentoxide tube as described on page 451 and caused a gain in weight of 2 mg. Unfortunately the importance of an accurate determination of the water allowed to pass by the sodium was not realised till after the apparatus was dismantled. There is, therefore, an uncertainty of several liters in the volume of the hydrogen and of a few tenths of a milligram in the weight of water. A correction of 3 mg. is applied to the total hydrogen of this series on account of this water. This raises the result of the series by 0.0096 H. I do not think the uncertainty attaching to the correction can exceed 0.003 H, and I believe that it is less than that.

Fourth Series.

It having been found that the tube of sodium wire does not completely dry the hydrogen passing over it, I determined to return to the phosphorus pentoxide and to make use of a preparation which had been sublimed in a current of oxygen, and which must, therefore, be free from phosphorus trioxide or any substance which could contaminate the hydrogen. A tube consisting of several parts fused together was prepared thus:



At *A*, *B*, *C*, and *D* were placed plugs of asbestos, while the portion from *C* to *D* was filled with phosphorus pentoxide. The tube was then placed in a combustion furnace and the portion from *B* to *C* was heated above the subliming point of the pentoxide. The portion from *C* to *D* was then gradually heated while a current of dry oxygen was passed through the tube. In this way the portion from *B* to *A* was partly filled with the pure pentoxide, free from the trioxide and from phosphoric acid. The tube was then cut off at *C*. Three tubes were filled in this way, and, when sealed together and to the tube filled with stick potash, these formed the drying apparatus used in the last series.

In this series four determinations were lost. Two of these were not completed; in one a little grease was carried away from the

stopcock during the expulsion of the water, and in one the platinised asbestos tube blew out. The experiment last referred to was continued and completed. There was, of course, some diffusion of water, carbon dioxide, nitrogen, and probably of carbon monoxide through the opening. On removal of the gases, about 8 mg. of nitrogen and one milligram of carbon dioxide were found. Supposing the carbon to have entered as carbon monoxide, which seems most probable, and applying the proper corrections, the result of the experiment is 15.892. This shows how perfectly the correction for nitrogen contained in the hydrogen can be applied.

The following summarised statement about the rejected experiments may be of interest. 28 experiments rejected or lost were carried at least as far as the weighing of the hydrogen. 8 of these were lost entirely. 4 of those made with manganese dioxide and lead chromate were grossly in error. Of the remaining 16, fifteen fall between the limits 15.97 and 15.83, and hence show a scarcely greater range than Dumas' best results. The mean of these 15 rejected experiments is 15.892.

The following are the detailed data for the individual series. The probable error of each series is given as the best criterion of the concordance of the results. The calculations have all been carried to the fourth decimal, to avoid, if possible, errors in the third decimal.

First Series.

	Gain.	Loss.	Nitrogen from the hydrogen.	Water by re-oxidation.	Corrected hydrogen.	Corrected oxygen.	Atomic weight.
1	0.9449	7.4785	0.0006	0.0215	0.9443	7.5000	15.885
2	0.6760	5.3521	0.0016	0.0034	0.6744	5.3555	15.882
3	0.7879	6.2432	0.0013	0.0137	0.7866	6.2569	15.909
4	0.5527	4.3483	0.0006	0.0420	0.5521	4.3903	15.904
5	0.4278	3.3366	0.0004	0.0631	0.4274	3.3997	15.909
6	0.8271	6.5437	0.0006	0.0249	0.8265	6.5686	15.895
	<u>4.2164</u>	<u>33.3024</u>	<u>0.0051</u>	<u>0.1686</u>	<u>4.2113</u>	<u>33.4710</u>	<u>95.384</u>

$$\text{Mean} = 15.8973 \pm 0.0032.$$

$$\frac{33.4710 \times 2}{4.2113} = 15.8958.$$

Second Series.

	Gain.	Loss.	Nitrogen from the hydrogen.	Water by re-oxidation.	Corrected hydrogen.	Corrected oxygen.	Atomic weight.
1	0.5054	4.0004	0.0010	0.0091	0.5044	4.0095	15.898
2	0.6328	5.0343	0.0003	0.0042	0.6325	5.0385	15.932
3	0.6356	5.0473	0.0007	0.0044	0.6349	5.0517	15.913
4	0.5576	4.4147	0.0012	0.0028	0.5564	4.4175	15.879
5	0.7339	5.8190	0.0004	0.0034	0.7335	5.8224	15.876
6	0.6706	5.3138	0.0010	0.0043	0.6696	5.3181	15.885
	<u>3.7359</u>	<u>29.6295</u>	<u>0.0046</u>	<u>0.0282</u>	<u>3.7313</u>	<u>29.6577</u>	<u>95.383</u>

$$\text{Mean} = 15.8971 \pm 0.0064.$$

$$\frac{29.6577 \times 2}{3.7313} = 15.8967.$$

Third Series.

	Gain.	Loss.	Nitrogen from the hydrogen.	Water by re-oxidation.	Corrected hydrogen.	Corrected oxygen.	Atomic weight.
1	0.9328	7.4004	0.0005	0.0073	0.9323	7.4077	15.891
2	0.9958	7.8976	0.0006	0.0069	0.9952	7.9045	15.885
3	0.3279	2.5950	0.0011	0.0027	0.3268	2.5977	15.898
4	0.7916	6.2725	0.0009	0.0073	0.7907	6.2798	15.884
5	0.7765	6.1598	0.0003	0.0073	0.7762	6.1671	15.891
6	1.1226	8.8921	0.0005	0.0210	1.1221	8.9131	15.887
	<u>4.9472</u>	<u>39.2699</u>	<u>0.0039</u>	<u>0.0525</u>	<u>4.9433</u>	<u>39.2699</u>	<u>95.336</u>

$$\text{Mean} = 15.8893 \pm 0.0014.$$

$$\text{Corrected mean} = 15.899 \text{ (see p. 454).}$$

$$\frac{39.2699 \times 2}{4.9403} = 15.8978 \text{ (see p. 454).}$$

Fourth Series.

	Gain.	Loss.	Nitrogen from the hydrogen.	Water by re-oxidation.	Corrected hydrogen.	Corrected oxygen.	Atomic weight.
1	1.0451	8.2814	0.0007	0.0203	1.0444	8.3017	15.898
2	0.7707	6.1089	0.0003	0.0144	0.7704	6.1233	15.896
3	0.8234	6.5335	0.0003	0.0086	0.8231	6.5421	15.896
4	0.8874	7.0376	0.0002	0.0114	0.8872	7.0490	15.890
5	0.9996	7.9312	0.0003	0.0091	0.9993	7.9403	15.892
6	1.1917	9.4403	0.0007	0.0192	1.1910	9.4595	15.885
	<u>5.7179</u>	<u>45.3329</u>	<u>0.0025</u>	<u>0.0830</u>	<u>5.7154</u>	<u>45.4159</u>	<u>95.357</u>

$$\text{Mean} = 15.8929 \pm 0.0013.$$

$$\frac{45.4159 \times 2}{5.7154} = 15.8925.$$

The mean of all the series, the third series being corrected as already stated, is 15.8965 ± 0.0017 . For the last twelve determinations the highest is 15.908 and the lowest 15.885. Ten of these last determinations fall between 15.890 and 15.901.

The result calculated from the sum of the hydrogen and the sum of the oxygen is $\frac{147.8145 \times 2}{18.5983} = 15.8955$.

I accept, therefore, as the most probable value which can be deduced from my work, the number **15.896**. The sources of error which I can see would indicate that the truth lies slightly below rather than above this value, but I do not speak with much confidence on that point.

Meyer and Seubert¹ have not long since expressed the opinion that the value 15.96 does not probably differ from the truth by more than 0.01 H. It seems to me that the facts now at our disposal do not justify such a conclusion. The determinations on which our knowledge of the constant in question rests are the older ones of Dumas, Erdmand and Marchand, and Regnault, and the more recent ones of Cooke and Richards, Lord Rayleigh, Scott, and Keiser. To these may, perhaps, be added determinations by Thomsen, and van der Plaats and the relation of silver to ammonium chloride and ammonium bromide, as found by Stas.

I would not say anything to detract from the esteem which is felt for the laborious and painstaking care with which Dumas conducted his determinations. But Dumas himself said² that he should consider himself very fortunate if the future should prove that his result was within one part in two hundred of the truth; that he had striven for an accuracy of one part in a thousand but could not attain it. It has been usually assumed that the errors of his method would tend to give a low rather than a high result. Professor Morley³ has called my attention to the fact that the hydrogen used by Dumas probably contained carbon from the zinc which he employed. Now, one-tenth mg. of carbon per liter of the hydrogen, if present in the form of a hydrocarbon, would cause the result found to be too high by about 0.05 H. The presence of a given amount of carbon would cause nearly three times as great an error by Dumas' method as by the method used by Cooke or by myself, and the error would be in the opposite direction.

¹ Ber. d. chem. Ges. 22, 874.

² Ann. Chim. Phys. 1843, 198.

³ See next article.

Erdmand and Marchand made two series of determinations, one of which gave the value 15.937 and the other 16.01. Unless some valid reason can be given for rejecting one or the other of these series, it is evident that their work leaves a very great uncertainty in the second decimal.

The ratio of densities as found by Regnault and corrected by Crafts¹ is 1:15.91. To derive the atomic weight from this we must know the ratio of combination for the gases. Scott² has worked carefully on this problem, but the last word that I can find from him is a statement³ that his earlier determinations were affected by a somewhat serious source of error. From Avogadro's law and the conduct of oxygen and hydrogen under changes of temperature and pressure, it seems probable that the ratio is at least as great as 2:1. The question is an experimental one, however, and I hope that we may soon have satisfactory evidence in regard to it. Scott has not determined whether the residual fixed gases of his experiments come from the oxygen or the hydrogen. As Morley⁴ has suggested, by the conversion of a part of the hydrogen into water by copper oxide and by the absorption of a part of the oxygen by metallic copper, it is possible to eliminate this uncertainty. Unless the uncertainty can be made very much smaller than it has been, it would seem that this should be done.

Cooke and Richards have obtained the value 15.869. In my first paper the opinion was expressed⁵ that the hydrogen used in their determinations must have contained nitrogen. In a more recent paper Cooke⁶ still maintains the purity of his hydrogen. While I should be loth to be drawn into any controversy with an investigator of such recognised ability and wide experience, my first statement still seems to me justifiable. The only evidence of the absence of nitrogen furnished in the papers referred to is that derived from the use of the spectroscope. But the evidence of the spectroscope is certainly not trustworthy in such a case until accompanied by some evidence as to the limit of the delicacy of the test when applied to the gases in question. The method which I have used enables me to detect nitrogen when there is only one part in thirty thousand by volume. It would seem desirable that such a test should be applied to the hydrogen furnished by the generator employed by Cooke and Richards.

¹ *Compt. Rend.* **106**, 1664.

² *Proc. Roy. Soc.* **42**, 396.

³ *Nature* **37** (1888), 439.

⁴ *This Journal* **10**, 23.

⁵ *This Journal* **11**, 161.

⁶ *Ibid.* **11**, 539.

Lord Rayleigh¹ has obtained the value 15.884 for the ratio of the densities of oxygen and hydrogen. He has also² obtained the value 15.89 for the atomic weight as determined by the direct combination of the elements. These results certainly indicate that the results obtained by Regnault and by Cooke and Richards cannot be so wide of the truth as Meyer and Seubert would have us suppose.

Among recent determinations, that of Keiser stands alone as approaching Dumas' value. When Keiser's paper first appeared I believed that the result which he had obtained must be very near the truth and I fully expected to obtain a similar result. After I became convinced by months of labor that the true value must be decidedly lower, I was led to re-examine the paper very carefully and I think there is one serious source of error in the determinations. A phosphorus pentoxide tube was interposed between the palladium and combustion tubes and the gain in weight of this tube was ascribed to water in the hydrogen. But the palladium tube had previously been exhausted and considerable hydrogen had been removed from it while under a very low tension. This should remove any moisture present also, and it would seem that the gain in the pentoxide tube must rather have come from the nitrogen, oxygen and air which also passed through the tube. This would seem the more probable if a few inches of rubber tubing were used for the passage of the gases, as would seem to be indicated by the diagram. Dr. Keiser informs me that without the correction referred to, the value would be between 15.92 and 15.93. There would still be a difference of about 0.025 H between his value and mine. As to this difference I am unable to offer any satisfactory explanation.

Van der Plaats states³ that by the combustion of known volumes (15 liters) of hydrogen he finds the value 15.94 to 15.96. I am unable to refer to the original paper, but, as the weight of the hydrogen was undoubtedly calculated from the old value obtained by Regnault, a correction must be applied and the value becomes 15.89 to 15.91.

Thomsen's value⁴ certainly requires this correction and then becomes 15.91. The amount of hydrogen burned was only one liter, however, in each determination, and the work was not intended as a determination of the atomic weight.

¹ Proc. Roy. Soc. **43**, 356.

² Ibid. **45**, 425.

³ Ann. Chim. Phys. 1886, **7**, 529.

⁴ Ber. d. chem. Ges. **3**, 928.

From the relation of silver to ammonium chloride and ammonium bromide as found by Stas and calculated by van der Plaats, the value 15.885 has been deduced,¹ but considerable uncertainty attaches to some of the data employed.

In conclusion I wish to express my hearty thanks to Professor Morley for the suggestions which have been referred to, and to Mr. W. B. Wiley who made the accompanying drawing.

ROSE POLYTECHNIC INSTITUTE, *May, 1890.*

CARBON AN IMPURITY IN HYDROGEN AFFECTING DETERMINATIONS OF ITS ATOMIC WEIGHT.

BY EDWARD W. MORLEY.

It is well known that metals prepared by the usual metallurgic processes contain gases. For instance, platinum or aluminum electrodes in a Plücker tube give off gas on heating by an electric discharge; wires of various metals enclosed in a vacuous space give off gas on heating by an electric current; in making certain castings, founders use artifices to prevent damage from gases remaining in the casting. It is therefore probable that zinc used in preparing hydrogen often contains imprisoned gases, and that hydrogen prepared from it often contains impurities whose nature and amount is of importance in attempting to determine the atomic weight of hydrogen. I published a brief statement of this source of error several years since, in an account of some of my analyses of air;¹ the published accounts of others engaged in determining the atomic weight of hydrogen have not noted the point, although it is well worthy of attention; so that it may not have been sufficiently taken into account.

1. When the purest zinc obtainable from manufacturers of pure chemicals is dissolved in dilute acids, the hydrogen produced usually contains carbon not readily removable by absorption and washing. I have tried many samples of expensive grades of zinc. If copper oxide be long heated in a current of oxygen it ceases to give off carbon dioxide. If then hydrogen be prepared as mentioned, and passed over the heated copper oxide, lime water soon

¹ Brauner, *Chem. News* 58, 307.

shows that carbon dioxide is produced. I have not yet obtained any zinc in commerce which failed to give a notable precipitate when ten or twenty liters of hydrogen prepared from it were so treated, and few in which half a liter did not give one.

2. When the purest commercial zinc is amalgamated and hydrogen obtained from it by electrolysis in the Bunsen decomposing cell, or in the modification of it used in my air analyses, and in the determination of the atomic weight of hydrogen by Cooke and by Rayleigh, the hydrogen often contains carbon. This I have proved by experiments like those last mentioned.

3. The purest zinc obtainable in commerce contains gases which are given off on melting it in a vacuum. Dr. W. H. Burton was so kind as to make a few experiments on this point. Such quantities as sixty and seventy grams of zinc, when heated to fusion in a well exhausted glass tube, gave off four or five cubic centimeters of gas. Part was carbon dioxide; after this was removed, explosion with oxygen produced from one-fifth to four-fifths of a cubic centimeter of carbon dioxide: part was nitrogen.

4. Hydrogen produced by the electrolysis of an alkaline hydroxide is likely to contain carbon, unless no alkaline carbonate is present. I tried for some time to obtain pure hydrogen by electrolysis of an alkaline solution. In the last experiment, when about abandoning the attempt for the present, I made a decomposing cell of clean glass and clean platinum, removed traces of organic matter by long treatment with chromic acid, and filled it with a solution of potassium hydroxide and potassium carbonate. When hydrogen was obtained from it by electrolysis and passed over heated pure copper oxide, baryta water was immediately rendered turbid. Unless, therefore, carbonic acid is removed from the alkaline solution in the voltameter, as by the use of barium hydroxide, hydrogen obtained from it cannot be assumed to be free from carbon.

5. It is probable that hydrogen obtained by acting on aluminum with an alkaline hydroxide would contain carbon; so probable that I have laid aside material and apparatus made ready for determinations of atomic weight with such hydrogen; but I have not yet found it worth while to *prove* the presence of such impurity.

6. Hydrochloric acid often contains organic matter; it is conceivable that hydrogen obtained by its use might contain carbon.

Sulphuric acid can be freed from carbon by distillation; but it is not so easy to purify hydrochloric acid if once contaminated. Hence, if one prepare zinc free from carbon by distillation in a vacuum, it may be convenient to use sulphuric acid instead of hydrochloric acid in preparing hydrogen from it. Dr. W. H. Burton has been so good as to prepare for me over a kilogram of zinc free from carbon.

The bearing of these facts on the determination of the atomic weight of hydrogen is obvious. If hydrogen containing carbon is weighed to determine its specific gravity, this will appear too large. If hydrogen containing carbon is weighed and burned, and the water produced is weighed, the atomic weight of hydrogen will appear too large. If hydrogen containing carbon is mixed with oxygen and exploded in the eudiometer, the combining volumes deduced will depend on the assumptions made as to the nature and source of the impurities remaining in the eudiometer. If weighed quantities of hydrogen containing carbon, and of oxygen are combined, oxygen will be wasted in oxidising the carbon, and the true weight of the hydrogen will be uncertain. If copper oxide is heated in a current of hydrogen containing carbon, oxygen will be consumed by the carbon, the carbon dioxide produced will be removed from the water by the prolonged current of hydrogen in which the reduced copper is cooled; so that the hydrogen as determined by difference will appear too small, and its atomic weight will be in defect.

The purity of the hydrogen used in a determination of its atomic weight must be proved, or else the impurity determined and a correction applied. If all impurities but nitrogen are removed, the residual nitrogen can be determined, although with some manipulative difficulty.

Since in a recent determination of the atomic weight of hydrogen it was sought to prove the purity of hydrogen by spectroscopic examination, it may be well to compare the delicacy of spectroscopic indications with that of gas analysis. With the spectroscope Best,¹ making the experiment at the suggestion of Sir Henry Roscoe, could not detect less than 0.011 nitrogen in hydrogen. Eudiometric analysis can detect far less. No very unusual manipulation will detect one part in a thousand; an apparatus permitting fractional explosion will detect and measure one part in ten

¹ Chem. News 55, 209.

thousand if it be provided with a sufficiently accurate means of reading volumes, and if the volumetric composition of water be first determined. And if a liter of hydrogen be passed into a vacuum containing pure hot copper oxide, and so be reduced to a volume of say ten cubic centimeters, then analysed in my eudiometer, it is possible to detect one part of nitrogen in more than one hundred thousand of hydrogen.

So far, by the electrolysis of dilute sulphuric acid, I have succeeded in obtaining hydrogen at a rate of ten and twenty liters an hour in which there is no carbon, no sulphur, in which, I believe, there is no oxygen, and in which the remaining nitrogen sometimes is too small to be detected by a process which readily detects one-hundredth of a cubic centimeter of nitrogen in a liter of hydrogen, and in which duplicate analyses agree within less than this amount. •

Contribution from the Chemical Laboratory of Clark University, Worcester, Mass. •

THE CONSTITUTION OF BENZOQUINONE.

By J. U. NEF.

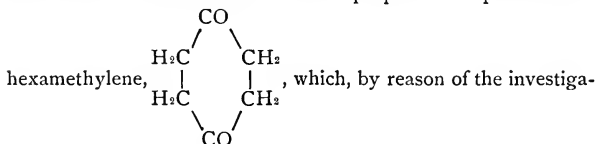
Although a large number of facts have become known concerning quinone and its derivatives, there are no reactions which can be regarded as decisively proving which of the three formulæ that have been put forward as representing the constitution of this substance is actually the correct one. In favor of the hyperoxide

formula,
$$\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{HC} \quad \text{O} \quad \text{CH} \\ | \quad | \quad | \\ \text{HC} \quad \text{O} \quad \text{CH} \\ \diagdown \quad \diagup \\ \text{C} \end{array}$$
, first advanced by Graebe,¹ is the fact that

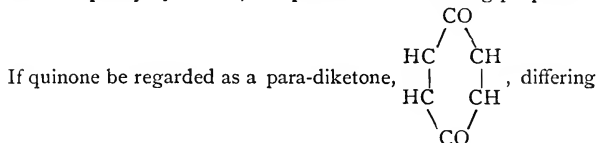
quinone by reduction takes up two and not four hydrogen atoms in the formation of hydroquinone. Further, the fact that on treatment with phosphorus pentachloride each of the oxygen atoms is replaced by one univalent chlorine atom, with formation of para-dichlorbenzene. Also a number of its properties are in

¹Ann. Chem. (Liebig) 146, 3.

favor of this formula. Quinone is a yellow substance, possessing a strong odor resembling chlorine, and it reacts as a powerful oxidising agent; it decomposes, for instance, hydrochloric and hydrobromic acid,¹ taking up the hydrogen and setting free chlorine or bromine. It behaves in this respect like hydrogen peroxide or its organic derivatives benzoyl- and acetyl-hyperoxide. In marked contrast thereto are the properties of para-diketo-



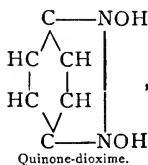
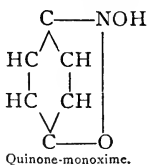
tion of v. Baeyer and Noyes,² is unquestionably to be regarded as a para-diketone. This substance is colorless, reacts with prussic acid and phenylhydrazine, and possesses no oxidising properties.



therefore from the substance just mentioned only in that it contains four hydrogen atoms less, it is very difficult to give an explanation for the totally different properties of the two compounds.

In favor of the ketone formula for quinone is the fact that it reacts with hydroxylamine, forming, according to Goldschmidt,³ a monoxime, and, as has been shown by Nietzki and Kehrman,⁴ a dioxime.

Since, however, these oximes can be derived from the hyperoxide formula as follows:



¹ Sarauw: *Ann. Chem. (Liebig)* **209**, 93; Levy and Schultz, *ibid.* **210**, 233.

² *Ber. d. chem. Ges.* **22**, 2168.

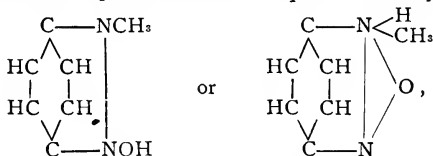
³ *Ibid.* **17**, 213.

⁴ *Ibid.* **20**, 614.

the formation of oximes does not prove the ketone nature of quinone. There are indeed many chemists who regard the fact

that methylaniline-nitrosamine, $\begin{array}{c} \text{C}-\text{N} \begin{array}{l} \diagup \text{NO} \\ \diagdown \text{CH}_3 \end{array} \\ \diagup \text{HC} \quad \diagdown \text{CH} \\ | \quad | \\ \text{HC} \quad \text{CH} \\ \diagdown \quad \diagup \\ \text{CH} \end{array}$ is converted by

means of alcoholic hydrochloric acid into *p*-nitroso-methylaniline,



as a proof of the existence of a binding between the two nitrogen atoms in the para position.

The instability of carboxylated derivatives¹ of benzoquinone, as well as also the ready elimination² of the halogen atoms in halogen substituted quinones, are points decidedly in favor of the ketone nature of quinone, since genuine benzene derivatives containing the carboxyl or halogen group are exceedingly stable.

Two ketone formulæ for quinone have been put forward; the

first, by Fittig and Siepermann,³ $\begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{HC} \quad \text{CH} \\ || \quad || \\ \text{HC} \quad \text{CH} \\ \diagdown \quad \diagup \\ \text{CO} \end{array}$, which assumes the

existence of two doubly bound carbon atoms. Later, Claus⁴ decided in favor of the existence of two para bonds, and suggested

the following formula, $\begin{array}{c} \text{C}=\text{O} \\ \diagup \quad \diagdown \\ \text{HC} \quad \text{CH} \\ | \quad | \\ \text{HC} \quad \text{CH} \\ \diagdown \quad \diagup \\ \text{C}=\text{O} \end{array}$.

¹Ann. Chem. (Liebig) **237**, 17.

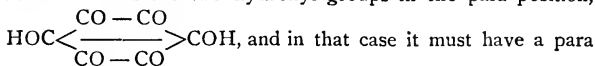
²Ann. Chem. (Liebig) **180**, 23.

³Ber. d. chem. Ges. **20**, 2027.

⁴J. prakt. Chem. [2] **37**, 461.

The majority of those who favor the ketone formula of quinone have unquestionably regarded Claus's diagonal formula as the more probable, since up to the present time no facts are known which point in any way to the existence of two doubly bound carbon atoms in quinone, unless perhaps the observation that thymoquinone¹ polymerises in the light.

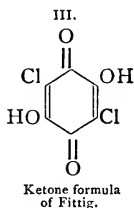
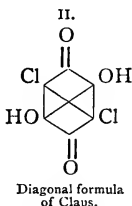
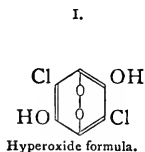
When one considers, on the other hand, that in the many reduced benzene derivatives there is not one in which a para binding exists, as has been conclusively proved by v. Baeyer's experiments, we have here again a strong argument against Claus's formula. Nietzki,² and with him also Claus, assumes that rhodizonic acid has the two hydroxyl groups in the para position,



bond. This has, however, not been proved by Nietzki's experiments, and the facts presented in the experimental part of this paper make it improbable that these groups are in the para position.

In order to settle definitely the question concerning the constitution of benzoquinone the study of the anilic acids seemed especially promising, and was begun with this object in view.

The first point to be determined was whether the two hydrogen atoms in the anilic acids can be removed by oxidation or not. It is necessary to state here that, as has been proved experimentally (see below), the hydrogen atoms in these acids are bound to oxygen, and not to carbon, as I supposed formerly,³ and that tautomerism is excluded in the anilic acid series. Chloranilic acid is therefore *p*-dichlor-dioxy-quinone, and we have the choice between the following three formulæ:



¹ Liebermann, Ber. d. chem. Ges. **10**, 2177; Liebermann and Ilinski, *ibid.* **18**, 3193.

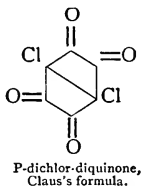
² Ber. d. chem. Ges. **18**, 1842.

³ This Journal **11**, 17.

Assuming formula I or II to be correct, there is no reason why the two hydrogen atoms should not be removed by oxidation. On this supposition the following products would be formed :



or

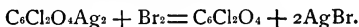


of which the latter would then represent dichlorrhodizonic acid.

The removal by oxidation of the two hydrogen atoms in chloranilic acid cannot be accomplished in this way, as my many fruitless experiments with this end in view prove ; and this is decidedly in favor of Fittig's formula. If we imagine in this formula the two hydrogen atoms to be absent, there is formed a compound which is just as incapable of existence as the radical methyl, since the valences set free at the carbon atoms containing chlorine cannot

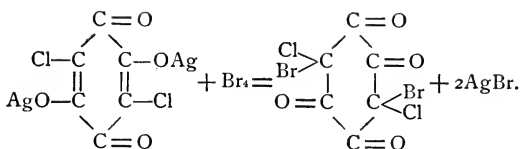
saturate one another. The compound, is not conceivable.

A diquinone, $C_6Cl_2O_4$, if it can be formed, must certainly be obtained by treating the dry silver salt of chloranilic acid with bromine according to the following equation :



I carried out this experiment and treated silver chloranilate with one and two molecules bromine, but invariably obtained as sole product a compound which proved to be dibrom-dichlor-tetraketo-hexamethylene. This is the case even when less than one molecule of bromine is used ; the only difference being that much silver chloranilate is left unchanged.

This reaction in the first place decides clearly in favor of Fittig's formula, and in the second place against the existence of a para bond ; the reaction takes place as follows :

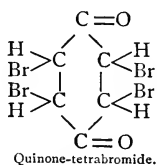
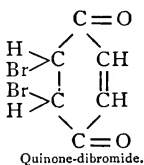
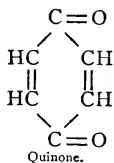


The hydroxyl groups in chloranilic acid can thus only be converted into quinone groups provided the valences set free at the two carbon atoms containing chlorine are correspondingly saturated. The valences cannot mutually paralyse one another, *i. e.* no union in the para position takes place; still less is it possible for these two carbon atoms to remain trivalent.

The behavior of the anilic acids is thus clearly in favor of Fittig's quinone formula, but the direct experimental proof that quinones have two doubly bound carbon atoms is yet wanting.

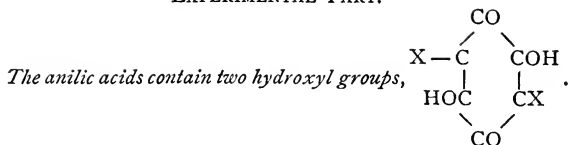
This it has been possible for me to furnish in a simple and most convincing manner in the case of quinone itself. This substance, namely, absorbs bromine with the same energy as ethylene itself without evolution of hydrobromic acid.

On adding one or two molecules of bromine to a solution of quinone in chloroform there is formed quinone dibromide and quinone tetrabromide.



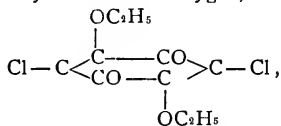
The proof that the addition products obtained have the above constitution is unquestionable, and the facts are thus so definitely and exclusively in favor of Fittig's formula that I regard a doubt concerning the constitution of benzoquinone as no longer admissible.

EXPERIMENTAL PART.

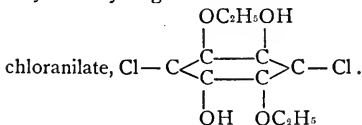


In my first paper¹ on the anilic acids I described many fruitless experiments to obtain alkyl or acid ethers of nitranilic acid. The intention thereby was to prove whether in the ethers the substituted group is bound to carbon or to oxygen, and thus to draw further conclusions concerning the position of the hydrogen atoms in the anilic acids themselves.

Such ethers are, however, easily obtained from chloranilic acid by means of its silver salt. Stenhouse² found, namely, that of allowing silver chloranilate to stand with ethyl iodide, ethyl chloranilate melting at 105° is formed. This ether, which both in appearance and behavior is a quinone, has unquestionably the alkyl groups bound to oxygen. This was proved by its behavior towards reducing agents. If, for instance, the alkyl groups were bound to carbon, $\text{C}_2\text{H}_5\text{Cl} > \text{C} < \begin{smallmatrix} \text{CO} - \text{CO} \\ \text{CO} - \text{CO} \end{smallmatrix} > \text{C} < \text{C}_2\text{H}_5\text{Cl}$, the substance must take up by reduction at least four hydrogen atoms; if on the other hand they are bound to oxygen,



only two hydrogen atoms can be added, forming ethyl hydro-



On treating a hot alcoholic solution of ethyl chloranilate with zinc-dust and hydrochloric acid or with sulphurous acid, there is always formed ethyl dihydro-chloranilate, melting at 152°. This

¹ This Journal 11, 17.

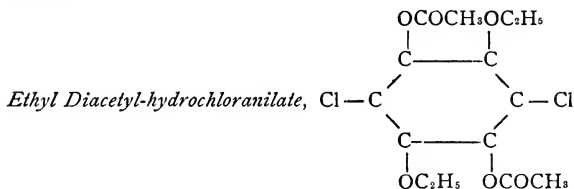
² Chem. Soc. Journal 23, 4, and Ann. Chem. (Liebig), Suppl. 8, 14.

substance has since been described by Kehrman.¹ The analysis of the compound dried at 110° gave the following result :

0.2128 gram substance gave 0.3485 gram CO₂ and 0.0908 gram H₂O.

	Theory for C ₆ $\left\{ \begin{array}{l} (\text{OH})_2 \\ (\text{OC}_2\text{H}_5)_2 \\ \text{Cl}_2 \end{array} \right.$	Found.
C	44.94	44.67
H	4.49	4.74

As regards the properties, etc., of the substance I refer to the paper of Kehrman.¹ Noteworthy concerning its behavior is the fact that the ether cannot be reduced further even after heating for six hours on a water-bath with sodium amalgam, as well as the fact that it can be boiled in alkaline solution if the air is excluded without the slightest change. Ethyl chloranilate, on the other hand, is saponified by simply adding dilute sodic hydrate to it. The ethers of oxyquinones thus are decidedly less stable than those of phenols, just as carboxylated and halogenated quinone derivatives are far more reactive than the corresponding genuine benzene derivatives.



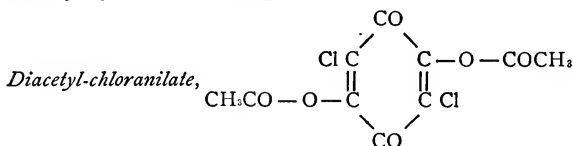
On heating ethyl hydrochloranilate (melting point 152°) for about three hours with acetic anhydride it is converted quantitatively into a diacetyl derivative, which, as it is difficultly soluble in boiling alcohol, is easily obtained pure. Twice recrystallised from alcohol, it was obtained in colorless four-sided prisms melting at 172°.

0.2198 gram substance dried at 110° gave 0.3826 gram CO₂ and 0.0911 gram H₂O.

¹ J. prakt. Chem. **40**, 373. In this connection I would like to state that Kehrman, in his last papers (J. prakt. Chem. **39**, 318; **40**, 365), describes experiments the carrying out of which I had by full right of priority reserved for myself (Ber. d. chem. Gesell. **20**, 2027; this Journal **11**, 17). Especially is this the case with his recent publication on the replacement of the chlorine atoms in chloranil.

Theory for $C_6 \left\{ \begin{array}{l} (OCOCH_3)_2 \\ (OC_2H_5)_2 \\ Cl_2 \end{array} \right.$		Found.
C	47.87	47.48
H	4.56	4.60

The compound is volatile without decomposition, and in alcoholic solution by means of alkalies is instantly converted back into ethyl hydrochloranilate again.



The direct proof that the anilic acids possess two hydroxyl groups has not yet been furnished by the isolation of a diacetyl derivative. The reason for this lies in the fact that the acetyl derivatives of oxyquinones are still less stable than those of phenols.

The diacetyl derivative of chloranilic acid can be obtained in the following way: Silver chloranilate (which was always prepared by adding a cold solution of the sodium salt to a solution of $1\frac{1}{2}$ times the calculated amount of silver nitrate and thereupon dried at 140°) is suspended in a small amount of ether (free from water and alcohol), and thereto twice the calculated amount of acetyl chloride, dissolved in ether, is added. The reaction is completed almost immediately, and in order to isolate the product formed the ether and excess of acetyl chloride is allowed to evaporate over sulphuric acid in a vacuum. The residue, after having been dried on clay plates, is extracted two to three times with warm, pure ether. After the ethereal solution has been concentrated by distilling off the ether in part, diacetyl chloranilate crystallises out in yellow needles, and the first portions separating out are perfectly pure; the later portions, however, are best crystallised from hot anhydrous benzene, from which, on cooling, the substance separates out in great part in the form of yellow needles.

0.2952 gram substance dried at 110° gave 0.4399 gram CO_2 and 0.0618 gram H_2O .

Theory for $C_6 \left\{ \begin{array}{l} O_2 \\ (OCOCH_3)_2 \\ Cl_2 \end{array} \right.$		Found.
C	40.95	40.67
H	2.05	2.36

The compound is volatile without decomposition, and melts at $182\frac{1}{2}^{\circ}$. Cold water has no effect on it, and boiling water converts it very slowly into chloranilic acid.

The substance is extremely unstable in alcoholic or acetic acid solution; it dissolves in alcohol at first with a yellow color, but even when only traces of water are present the solution, slowly on standing, instantly on heating, becomes colored violet. On adding water to the alcoholic solution, saponification to chloranilic acid and acetic acid takes place instantly. For recrystallising the diacetyl derivative, therefore, only such solvents can be used which contain no water and also do not absorb water.

The above facts, namely:

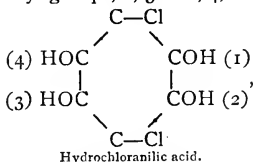
(1) That ethyl chloranilate takes up only two hydrogen atoms by reduction;

(2) That this substance is saponified by dilute sodium hydrate in the cold;

(3) That an acetyl derivative of chloranilic acid has been obtained,

prove that in the ethers of chloranilic acid the substituted group is bound to oxygen. The conclusion that the salts as well as the acid itself have an analogous constitution is justifiable; the latter therefore possesses two hydroxyl groups.

Remarkably enough, it is impossible to remove the hydrogen atoms from the two hydroxyl groups by oxidising agents, and this led me at first to the thought that perhaps the two pairs of hydroxyl groups in hydrochloranilic acid possessed different functions. It was therefore necessary to prove that it is indifferent which pair of hydroxyl groups, 1, 3 or 2, 4,

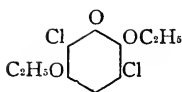


Hydrochloranilic acid.

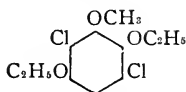
are converted by oxidation into the quinone group.

To decide this I proceeded as follows:

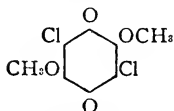
Chloranilic ethyl ether was reduced and the hydroquinone thus obtained converted into the methyl ether. In like manner chloranilic methyl ether was reduced and the hydroquinone obtained converted into the ethyl ether.



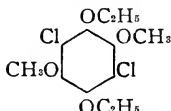
Starting point.
Chloranilic ethyl ether.



End product.
Methyl hydrochloranilic ethyl ether.



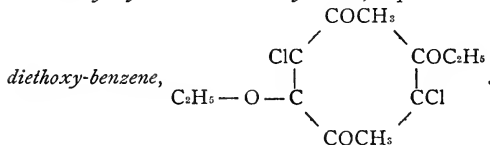
Starting point.
Chloranilic methyl ether.



End product.
Ethyl hydrochloranilic methyl ether.

If there were a difference of any kind between the pairs of hydroxyl groups the two end-products obtained must be isomeric; they were, however, found to be identical in every respect, and by oxidation with nitric acid both are converted into a mixture of ethyl and methyl chloranilate. Therefrom I draw the conclusion that the reason for the fact that the two remaining hydrogen atoms in hydrochloranilic acid cannot be removed by oxidation lies not in any difference between the pairs of oxygen groups in the para position, but that it is to be sought in the grouping of the carbon atoms forming the closed chain.

Dimethyl hydrochloranilic ethyl ether, or p-Dichlor-dimethoxy-



If ethyl hydrochloranilate be heated for one day in alcoholic solution with caustic potash and methyl iodide ($1\frac{1}{2}$ times the calculated amount) in a sealed tube at 100° , the two hydrogen atoms are replaced by methyl. After adding water, the product formed is extracted with chloroform and this solution washed with sodic hydrate and water. The chloroform solution, after having been dried with calcium chloride, is distilled off, and the residue recrystallised from dilute methyl alcohol. Thus colorless, long, flat needles were obtained, which melt at 103° and are volatile without decomposition. The yield was 1.5 gram from 2 grams hydroquinone taken.

I. 0.2286 gram substance, dried over sulphuric acid in a vacuum, gave 0.4070 gram CO_2 and 0.1130 gram H_2O .

II. 0.2109 gram substance gave 0.3742 gram CO_2 and 0.1104 gram H_2O .

III. 0.1336 gram substance gave 0.1304 gram AgCl (Carius).

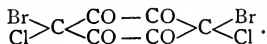
Theory for $C_8 \begin{cases} (OCH_3)_2 \\ (OC_2H_5)_2 \\ Cl_2 \end{cases}$		I.	Found.	II.
C	48.81	48.55		48.39
H	5.40	5.51		5.89
Cl	24.07	24.15		

The substance is easily soluble in organic solvents. It can be boiled in alcoholic solution with sodic hydrate without change. Also reducing agents, as zinc dust and hydrochloric acid or sodium amalgam, cause no change even after long treatment in hot alcoholic solution. On dissolving the substance in fuming nitric acid, oxidation immediately takes place and water precipitates a yellow, flaky product which consists of a mixture of methyl and ethyl chloranilate. These can be separated by fractional crystallisation from methyl or ethyl alcohol, since the methyl ether is more difficultly soluble. The products obtained were in every respect identical with the corresponding ethers formed from silver chloranilate and methyl or ethyl iodide. Methyl chloranilate (melting point 142°) has recently been made in this way by Kehrmann.¹

Finally, methyl chloranilate (made from the silver salt with methyl iodide) was converted into the hydroquinone,² melting point 196°, and this converted into the ethyl ether by heating for a day in a sealed tube at 100° with ethyl alcohol, caustic potash and ethyl iodide. The ethyl hydrochloranilic methyl ether thus obtained was in every respect identical with the above methyl hydrochloranilic ethyl ether melting at 103°.

HEXAMETHYLENE DERIVATIVES FROM THE ANILIC ACIDS.

Dibrom-dichlor-tetra-keto-hexamethylene,



As already mentioned in the introduction, many experiments were carried out in order to remove the two hydrogen atoms in

¹ J. prakt. Chem. **40**, 370.

² Ibid. 40, 374.

chloranilic acid by oxidation, in order thus to obtain a diquinone $C_6Cl_2O_4$. In all the experiments with the most varied oxidising agents the substance was either left unchanged or entirely decomposed. In order finally to attain my object I attempted to remove the metal from the salts of the acid by means of bromine. The salt best adapted to this purpose is the silver salt, which was prepared as mentioned above under diacetyl chloranilic acid. It was suspended in pure anhydrous carbon bisulphide, and thereto was slowly added (care being taken to shake thoroughly) a dilute solution of bromine in carbon bisulphide solution. The reaction takes place instantly and is completed only after exactly two molecules of bromine have been added—a fact which in itself points to the conclusion that bromine has been taken up in the reaction product formed. Bromine acts in an analogous manner on the anhydrous sodium salt, but in this case the reaction takes place very slowly and is completed only after twenty-four hours.

The silver bromide is filtered off, and after distilling off a portion of the carbon bisulphide filtrate until crystals are seen at the sides of the flask, there separates out on cooling a large quantity of pale yellow, flat needles. These after being recrystallised once from carbon bisulphide were pure.

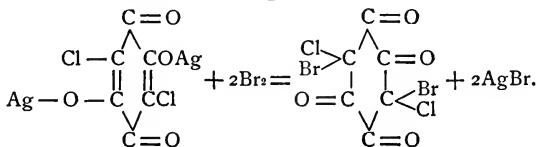
I. 0.3020 gram substance, dried over sulphuric acid in a vacuum, gave 0.2165 gram CO_2 and 0.0131 gram H_2O .

II. 0.3116 gram substance gave 0.2220 gram CO_2 and 0.0081 gram H_2O .

III. 0.2095 gram substance gave 0.3760 gram $AgCl$, $AgBr$, instead of 0.3784 gram $AgCl$, $AgBr$ calculated.

	Theory for $C_6Br_2Cl_2O_4$.	I.	Found.	II.
C	19.62	19.53		19.43
H	0.00	0.48		0.29
Br	} 62.91	62.54		...
Cl				

Dichlor-dibrom-tetra-keto-hexamethylene has therefore been formed according to the following reaction:



A small quantity of the substance heated quickly in a test-tube melts sharply and then sublimes in flat needles or in cubes. Heated slowly in a capillary tube it begins to soften and decompose at 110° , and finally melts completely at 160° , decomposing with marked evolution of gas. It has a piercing odor.

Crystallised from carbon disulphide, in which it dissolves with pale yellow color and green fluorescence, the substance is obtained in long, flat, pale yellow needles, in six-sided plates or in cubic-like forms. The crystals are very hygroscopic and therefore lose their luster very quickly in the air, so that a goniometric measurement is not possible. The substance crystallises also very well from ether (free from alcohol and water), but it seems slowly (in 24 hours) to decompose the ether, since much hydrobromic acid is set free. A carbon disulphide solution of the tetra-keto derivative can be heated for a long time at 100° with molecular silver without change, and even when heated for two hours at 150° it was only very slightly decomposed.

On treating an ethereal solution with phenylhydrazine there is formed a yellow, flaky precipitate, which can be obtained in colorless pearly scales by recrystallisation from acetic acid. The product, however, is not a hydrazone, but an unstable addition product (various analyses gave figures from which it is impossible to deduce a formula), which is immediately decomposed by water with liberation of phenylhydrazine. It was also impossible to obtain with *o*-toluylene-diamine a quinoxaline derivative, although a dirty dark-brown precipitate results on adding this reagent to an ethereal solution of the tetra-keto compound. In the absence of water, therefore, the compound is tolerably stable, but if water be present it is very quickly decomposed. On pouring a small amount of water over the solid substance, marked evolution of heat and of carbonic anhydride are noticeable. The substance dissolves in much water, with yellow color and green fluorescence, and then slowly evolution of carbonic anhydride takes place.

When the decomposition is completed, ether extracts from the aqueous solution no longer the hexamethylene derivative, but a yellowish oil, which is an acid and forms an ammonium salt that crystallises well. The same oil is formed directly from chlor-anilic acid salts (sodium or potassium salt), if these in solution be treated with two molecules of bromine water. The hexamethylene derivative, which must be formed as the intermediate product,

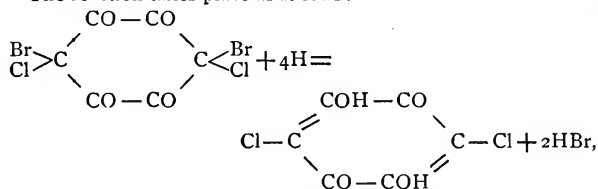
can thus in fact not be isolated at all by this method. This reaction, whereby penta-methylene derivatives are formed, will be explained later. The penta-methylene compounds here formed, of which two possibly may be present, were not investigated further.

Dichlor-dibrom-tetra-keto-hexamethylene is very easily converted back into chloranilic acid by means of sulphurous acid. The substance is best added in small portions to an aqueous solution of sulphurous acid, whereby chloranilic acid immediately separates out completely. The reduction never takes place quantitatively, since a partial conversion into the penta-methylene derivative cannot be prevented. From 1 gram substance in the most favorable case, 0.2 gram chloranilic acid containing water of crystallisation was obtained.

A halogen determination proved that the substance was pure chloranilic acid, containing not a trace of bromanilic acid.

0.1136 gram substance dried at 130° gave 0.1550 gram AgCl; calculated, 0.1560 gram AgCl. Therefrom (0.1550 gram AgCl) was obtained by heating in an atmosphere of hydrogen 0.1159 gram Ag, instead of 0.1166 gram Ag, calculated for AgCl.

The reaction takes place as follows:



whereby the bromine atoms are split off by preference.

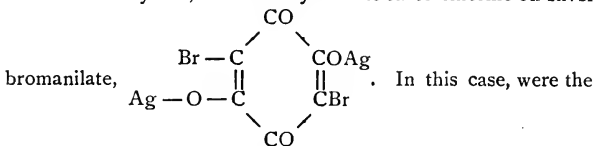
That the substance possesses the constitution

$\text{Br} > \text{C} < \begin{array}{c} \text{CO}-\text{CO} \\ \diagup \quad \diagdown \\ \text{CO}-\text{CO} \end{array} > \text{C} < \text{Br}$ and is not an ether of hypobromous

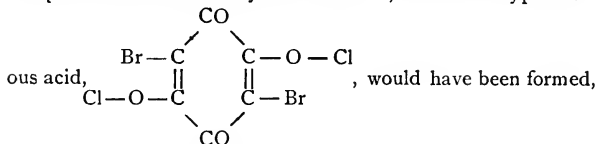
acid, $\begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{Cl} \text{ C} \quad \text{C} \text{ O}-\text{Br} \\ \diagdown \quad \diagup \\ \text{Br}-\text{O}-\text{C} \quad \text{C} \text{ Cl} \\ \diagup \quad \diagdown \\ \text{CO} \end{array}$, is proved even by the com-

paratively great stability of the substance in the absence of water; furthermore, such an ether must undoubtedly give with water chloranilic acid.

A further proof for the constitution of the substance as given above is the following: The *same substance*, dichlor-dibrom-tetra-keto-hexamethylene, is formed by the action of chlorine on silver



compound not a hexamethylene derivative, an ether of hypochlor-

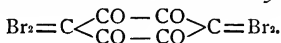


and this must unquestionably be readily converted into bromanilic acid.

Since the two products, however, are identical, a new proof is won for the constitution of the substance as given.

The observation that the compound under discussion gives pure chloranilic acid by reduction with sulphurous acid is noteworthy. The chlorine atoms must, therefore, be more firmly bound to carbon than the bromine atoms. In favor of this explanation is the fact that tetrachlor-tetraketo-hexamethylene, obtained from silver chloranilate with chlorine, is *not* converted back into chloranilic acid by means of sulphurous acid.

Tetra-brom-tetra-keto-hexamethylene,



This substance was obtained from silver bromanilate by means of bromine, and the preparation and purification is exactly the same as with the above dibrom-dichlor derivative. It crystallises in pale yellow flat needles, which, analysed, gave the following result:

0.2467 gram substance, dried over sulphuric acid in a vacuum, gave 0.1430 gram CO_2 and 0.0105 gram H_2O .

0.1636 gram substance gave 0.2678 gram AgBr (Carius).

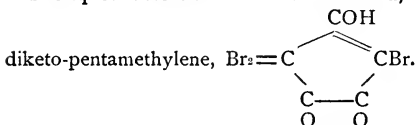
	Theory for $C_6Br_4O_4$.	Found.
C	15.79	15.81
H	0.00	0.47
Br	70.18	69.54

When heated slowly the substance shows exactly the same behavior as dibrom-dichlor-tetra-keto-hexamethylene; heated quickly it cannot, however, be sublimed without decomposition as is the case with the latter. It has a sharp piercing odor.

Sulphurous acid naturally converts the compound back again into bromanilic acid; the behavior of the substance towards water must be discussed at some length.

On pouring a small amount of water over the solid substance a violent reaction, accompanied by marked evolution of heat and of carbonic anhydride, takes place, just as is the case when a mineral acid is added to a carbonate.

The aqueous solution now contains an acid, namely tribrom-oxy-



In order to isolate it, the solution is acidified with sulphuric acid and repeatedly extracted with ether. The product obtained after evaporating the ether was purified according to the directions given by Hantzsch¹ (who obtained it from potassic bromanilate by means of bromine in caustic potash solution), namely, through the ammonium salt. It was then completely analysed.

0.2966 gram substance, dried over sulphuric acid in a vacuum, gave 0.1853 gram CO_2 and 0.0152 gram H_2O .

0.1168 gram substance gave 0.1886 gram $AgBr$ (Carius).

	Theory for $C_6HO_3Br_3$.	Found.
C	17.19	17.02
H	0.29	0.57
Br	68.70	68.70

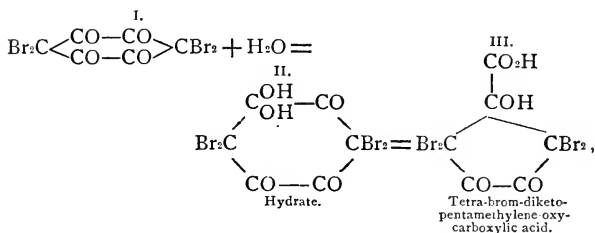
Since the substance is a monobasic acid, it is better to regard it as tribrom-oxy-diketo-pentamethylene and not as tribrom-triketo-pentamethylene, as Hantzsch assumes.

An experiment to determine the amount of carbonic anhydride given off in the formation of this substance proved that one molecule is split off.

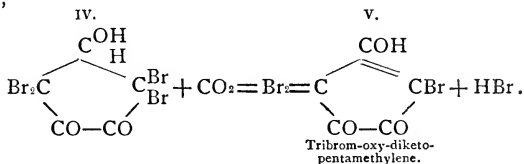
¹ Ber. d. chem. Ges. 21, 2440.

1.6728 gram substance (tetrabrom-tetraketo derivative) gave, when treated in a flask with a small amount (30-50 cc.) of water after expelling the carbonic anhydride formed with air, 0.1460 gram CO_2 instead of 0.1614 gram calculated. A small loss of carbonic anhydride was unquestioned, since the experiment was not carried out with all possible precautions.

The reaction probably takes place as follows :



which spontaneously loses carbonic anhydride and hydrobromic acid,



The explanation of the mechanism of the reaction as given is based upon Zincke's experiments with β -naphtho-quinone, where, by means of alkalis, the conversion of the ortho-diketone group into the oxy-carboxyl group takes place; it is justifiable as well in this case since we have to do with a diortho-diketone, but the intermediate products II-IV are here not capable of existence.

Remarkable is the fact that the conversion into the pentamethylene derivative is here caused almost instantly by *pure water*. This proves better than any fact yet known the great tension existing in the hexamethylene ring and the tendency to go over into the stable pentamethylene ring. The "tension theory" of v. Baeyer² receives thereby a new very convincing experimental proof.

¹ Ber. d. deutsch. chem. Gesell: **19**, 2500; **20**, 1265.

² Ibid. **18**, 2277.

Tribrom-oxy-diketo-pentamethylene is also formed quantitatively by treating an aqueous solution of potassium or sodium bromanilate with two molecules of bromine water.

It is a well known fact that the anilic acids, as well as their salts,¹ are converted by means of oxidising agents, especially by means of halogens in the presence of water, into fatty compounds or pentamethylene derivatives. The mechanism of these reactions has heretofore not been understood, for the reason that the first intermediate products formed, namely, the tetra-keto-hexamethylene derivatives, were not isolated, since the oxidation was carried out in aqueous solution, in which, as we now know, they are instantly decomposed.

Thus Hantzsch describes in his first paper,² "Ueber Spaltungsprodukte der Chlor- und Bromanilsäure," a substance which he calls bromanilic acid-bromide, and later,³ by reason of my paper in this Journal, Vol. **II**, p. 26, he considers it to be tetra-brom-tetra-keto-hexamethylene. It is, however, impossible that this chemist could have obtained this compound by his method of preparing the substance, since the tetrabrom derivative is, as I have shown, almost instantly decomposed by water, and, furthermore, possesses entirely different properties from those shown by Hantzsch's product. I have therefore repeated his experiments and think that the product first described as bromanilic acid bromide was nothing but tribrom-oxy-diketo-pentamethylene, which contains at first an equal amount of bromanilic acid, and after its purification must have still contained traces of bromanilic acid. The melting point (184° – 186°), as well as the analysis (percentage of bromine found = 69; percentage calculated = 68.8), agrees well for the pentamethylene derivative, which, when perfectly pure, melts at 191° .

On treating silver chloranilate, suspended in pure carbon bisulphide, with *dry* chlorine until about three-fourths of the silver salt has been changed into silver chloride, tetra-chlor-tetra-keto-hexamethylene was obtained, after concentrating the carbon bisulphide filtrate, in the form of pale yellow needles fully a centimeter in length. The substance is volatile without decomposition and sublimes in yellow needles which have a piercing odor. It is,

¹ Hantzsch: Ber. d. chem. Gesell. **21**, 2439; **22**, 2841; Hantzsch and Zeckendorff: Ber. d. chem. Gesell. **20**, 1308; Levy and Jedlicka: Ann. Chem. (Liebig) **249**, 66; Nef, this Journal **11**, 17.

² Ber. d. chem. Gesell. **21**, 2439.

³ Ibid. **22**, 2845.

however, so very hygroscopic that it deliquesces in a very short time in the air, and even when kept in a desiccator it slowly decomposes. I regarded an analysis of it as superfluous, and in any case it would be very difficult to carry out.

Tetra-chlor-tetra-keto-hexamethylene, $\text{Cl}_2\text{C} \begin{smallmatrix} \diagup \text{CO} - \text{CO} \diagdown \\ \diagdown \text{CO} - \text{CO} \diagup \end{smallmatrix} \text{CCl}_2$, behaves towards water exactly as the corresponding tetra-bromine derivative, and thus trichlor-oxy-diketo-pentamethylene,

$\text{Cl}_2\text{C} \begin{smallmatrix} \diagup \text{COH} = \\ \diagdown \text{CO} - \text{CO} \diagup \end{smallmatrix} \text{C} - \text{Cl}$, was obtained. As regards its prop-

erties, as well as those of the ammonium salt, I can confirm the statements of Hantzsch,¹ who obtained it in a different way. As already mentioned, tetra-chlor-tetra-keto-hexamethylene differs from the corresponding tetrabrom- and dibrom-dichlor derivative in its behavior towards sulphurous acid, which in this case does not convert it into chloranilic acid. This is due to the fact that the chlorine atoms are bound more firmly to carbon, and therefore the fact that dibrom-dichlor-tetra-keto-hexamethylene gives by reduction with sulphurous acid pure chloranilic acid, is now no longer surprising.

The conversion of the tetrachlor derivative into hydrochloranilic acid is, however, possible if more powerful reducing agents be taken, as zinc dust and acetic acid.

From the explanation given above of the conversion of the tetra-keto-hexamethylene into pentamethylene derivatives, it follows that tetra-chlor-diketo-pentamethylene-oxycarboxylic acid, which in all probability must have been formed as an intermediate product (III), is not capable of existence.

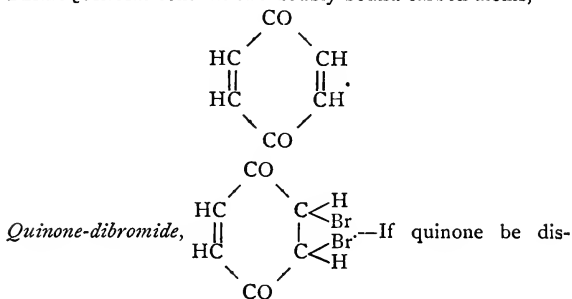
Now, Hantzsch² describes this compound as an especially stable product, and I therefore believe that the substances which this chemist has obtained by the action of hypochlorous acid salts on chloranilic acid, must possess a different constitution from that at present given to them.

Finally, I would state that this investigation also confutes the assumption of the existence of tautomerism in the anilic acid series. The experiments prove that the metal in the anilic acid salts is bound to oxygen, and the hydroxyl formula suffices to explain fully and simply all the reactions shown by these acids.

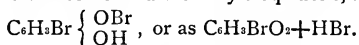
¹ Ber. d. chem. Gesell. **21**, 2435.

² Ibid. **22**, 2846.

BENZOQUINONE contains two doubly bound carbon atoms,



solved in dry chloroform and a 5 per cent. solution of bromine in chloroform be added, all the bromine is instantly absorbed without the slightest evolution of hydrobromic acid. After one molecule of bromine has been added the yellow solution is allowed to evaporate spontaneously, and a substance possessing a high specific gravity and crystallising in flat needles is obtained, which after pulverising and washing with little alcohol is obtained pure. It melts at 86° and can also be purified by dissolving in chloroform and precipitating with petroleum ether (boiling point 40° – 50°). This substance has long been known (since 1881), but because of its peculiar behavior Sarauw,¹ who discovered it, regarded it as an isomeric dibrom-hydroquinone, as



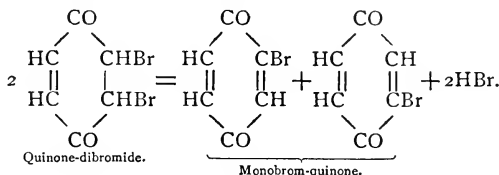
Hereby is again appended the analysis of Sarauw:

Theory for $\text{C}_6\text{H}_2\text{O}_2, \text{Br}_2$.		Found.
C	26.86	26.89
H	1.41	1.66
Br	59.70	60.03

As regards its properties I can confirm the statements of Sarauw; the substance, which has a pale yellow color, possesses, however, a distinct greenish tint, since the solutions also are colored greenish yellow, and it also has a distinct but faint odor of quinone. The following concerning its behavior is noteworthy: The substance dissolves easily, in the cold, in fuming nitric acid, and can be precipitated again unchanged by the addition of water

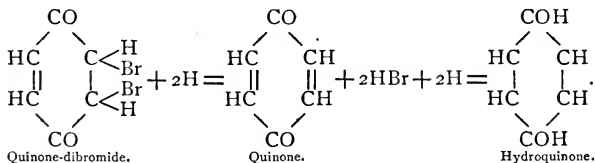
¹ Ann. Chem. (Liebig) 209, 111.

even after boiling with nitric acid. It is insoluble in cold water; on boiling with water hydrobromic acid is slowly and quantitatively split off, and, on cooling, monobrom-quinone¹ (melting point 56°) crystallises out. The same reaction takes place on heating the substance in solution as was proved in the case of an alcoholic and an acetic acid solution.



Hydrobromic acid is evolved when the solid substance is heated very slightly above its melting point. If the temperature be low and the substance heated carefully, monobrom-quinone is formed; at a higher temperature much *p*-dibrom-hydroquinone² (melting point 186°) is formed. The monobrom-quinone thus formed at first oxidises the hydrobromic acid, forming monobrom-hydroquinone, which is then instantly converted by the bromine set free into *p*-dibrom-hydroquinone (*vide* Sarauw: Liebig's Annalen **209**, 108).

All these reactions *seem* to point to the fact that in quinone-dibromide one bromine atom is more firmly bound than the other. This, however, is not the case. If quinone-dibromide be dissolved in acetic acid and zinc dust be added, and finally the solution be heated gently, there is formed quantitatively pure hydroquinone (melting point 169°).



The two bromine atoms added in the ortho position are thus removed and the double bond again restored, just as v. Baeyer³

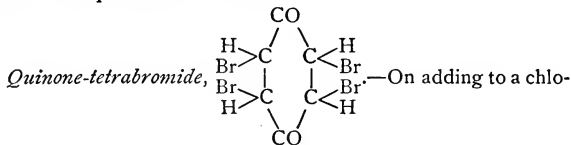
¹ Sarauw: Ann. Chem. (Liebig) **209**, 106.

² Ibid. **209**, 109.

³ Ann. Chem. (Liebig) **245**, 103; **251**, 261.

found to be the case with his ortho-dibrom addition-products of hydrogenated terephthalic acids.

Quinone-dibromide is decomposed by sodic hydrate with marked evolution of heat and deep brown coloration; on adding an acid to the solution obtained a brown flaky substance is precipitated. Very noteworthy is the above mentioned stability towards fuming nitric acid, a fact which is also so noteworthy in the cases of quinones themselves.



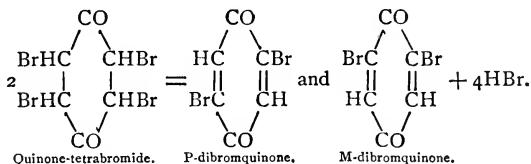
roform solution of quinone two molecules of bromine (5 per cent. solution in chloroform), or to a chloroform solution of quinone-dibromide one molecule of bromine, decoloration sets in at first almost immediately, but finally very slowly, and there soon separates out a colorless product in the form of very heavy scales. If the bromine solution contains some hydrobromic acid the absorption of the bromine is immediate, as well as also the separation of the colorless product. In the absence of hydrobromic acid it is several hours before complete absorption of bromine takes place, but very soon (in about 20 minutes) quinone-tetrabromide begins to crystallise out in colorless pearly scales. These can be filtered off directly without waiting for the total absorption of the bromine, and, after washing repeatedly with cold chloroform, they are perfectly pure. In the preparation as given above, at first not the slightest trace of hydrobromic acid is noticeable, and only towards the end are small quantities apparent. The yield of tetrabromide is 4.5–5 grams from 3 grams quinone (calculated 11.9 grams). Thus, while in the case of the dibromide the yield is almost quantitative, in this case secondary reactions also take place. The analysis of the substance washed repeatedly with chloroform gave the following result :

0.4976 gram substance, dried over sulphuric acid in a vacuum, gave 0.3058 gram CO_2 and 0.0486 gram H_2O .

0.2008 gram substance gave 0.3498 gram AgBr (Carius).

	Theory for $\text{C}_6\text{H}_2\text{O}_2\text{Br}_4$.	Found.
C	16.82	16.76
H	0.93	1.08
Br	74.77	74.12

The substance is very difficultly soluble in the cold in all solvents; on heating in solution, hydrobromic acid is split off. The solid substance decomposes also in the same way if kept for a time in closed vessels. In attempting to determine the melting point a yellow coloration becomes noticeable at 110° , which constantly becomes more intense until finally the substance melts between 170° – 175° with marked evolution of hydrobromic acid. Two molecules of hydrobromic acid can be split off quantitatively as follows: quinone-tetrabromide is suspended in alcohol containing about 10–15 per cent. water, and the solution heated to the boiling point; the tetrabromide dissolves slowly with yellow coloration, and on addition of water a yellow product is precipitated, which is a mixture of about equal parts of meta- and para-dibromquinone. The separation of these isomers could readily be accomplished, since para-dibromquinone is much more difficultly soluble in ether than the meta compound. Thus the para derivative,¹ melting at 188° , was obtained, and for further identification it was converted into the hydroquinone² (melting point 187°). The meta-dibromquinone obtained (melting point 122°) was found to be identical with the product obtained by Levy and Schultz³ from tribromphenol. The reaction therefore takes place as follows:



Quinone-tetrabromide thus exactly as the dibromide has a great tendency to split off hydrobromic acid. The above reaction also takes place on heating the solid substance directly; in this case, however, it is necessary to heat very carefully (not higher than 120°), otherwise the isomeric dibromquinones first formed act on the hydrobromic acid and tri- and tetra-bromhydroquinone result. If, for instance, quinone-tetrabromide be heated to its melting point hydrobromic acid is given off rapidly, and at the same time a small amount of bromine is set free. The residue now consists

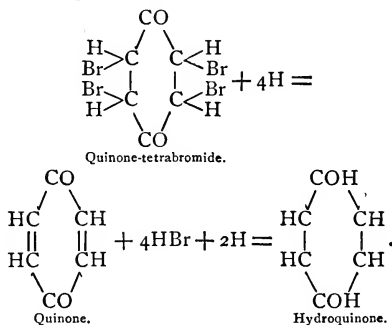
¹ Sarauw: Ann. Chem. (Liebig) **209**, 113.

² Ann. Chem. (Liebig) **209**, 109.

³ Ann. Chem. (Liebig) **210**, 159.

in great part of tribromhydroquinone with some tetrabromhydroquinone. The formation of these substances is easily explained when one considers that dibromquinone is converted by hydrobromic acid into tribrom- and tetrabromhydroquinone.¹

These facts *seem* again to point to the conclusion that in quinone-tetrabromide two bromine atoms are more firmly bound than the other two. This is, however, only apparent. On treating quinone-tetrabromide with zinc dust and acetic acid there is formed quantitatively pure hydroquinone, melting point 169°, according to the equation :



The pairs of bromine atoms added in the ortho position are thus removed just as in the case of quinone-dibromide, and the double bonds again restored. Sodid hydrate decomposes quinone-tetrabromide with marked evolution of heat and deep brown coloration. The tetrabromide also resembles the dibromide in its behavior towards fuming nitric acid, in which it is insoluble in the cold, but on warming it dissolves in very small amount, and on cooling it crystallises out again unchanged in colorless scales.

The above facts prove unquestionably that quinone adds two and four atoms of bromine, forming addition products which show a remarkable but now readily comprehensible behavior. Quinone is *yellow*, and has a *strong smell*; quinone-dibromide, *pale yellow* with a greenish tint and *faint odor*; quinone-tetrabromide, which is nothing but tetrabrom-*p*-diketo-hexamethylene, is *colorless* and *inodorous*, just as *p*-diketohexamethylene itself.²

¹ Sarauw: Ann. Chem. (Liebig) **209**, 117.

² Herrman: Ann. Chem. (Liebig) **211**, 332; v. Baeyer and Noyes; Ber. d. chem. Ges. **22**, 2168.

The experiments with quinone-di- and tetrabromide, as well as experiments to convert nitranilic acid and quinone-dioxyterephthalic ether into hexamethylene and pentamethylene derivatives, according to the method discovered above, will be continued.

In these experiments I have again been most zealously assisted by Dr. V. Paepcke, to whom I here express my warmest thanks.

WORCESTER, MASS., *May* 30, 1890.

ON THE ACTION OF METALLIC CADMIUM ON THE HALOGEN SALTS OF CADMIUM, AND ON THE SUB-HYDROXIDE AND SUB-OXIDE OF CADMIUM.

BY H. N. MORSE AND H. C. JONES.

If anhydrous chloride of cadmium is heated with metallic cadmium, in a vacuum or in an atmosphere of nitrogen, to the fusing point of the chloride, the molten salt quickly assumes a fine garnet red color. In order to investigate this phenomenon we prepared a quantity of the chloride by dissolving the redistilled metal in hydrochloric acid, evaporating to dryness with an excess of the acid, and distilling the residue in a current of dry hydrochloric acid gas. For the purpose of distillation, a long platinum boat containing the chloride was placed in a combustion tube and heated in a current of the acid gas until the material had disappeared from the boat and collected upon the bottom of the glass tube. The chloride, thus freed from water and oxychloride, and an excess of metal were placed in a long-necked flask of hard glass, and, after displacement of the air by nitrogen, heated to the melting point of the chloride. The liquid chloride attained its maximum depth of color within a few minutes, nevertheless the heating was continued for five hours. It was observed that globules of metal collected upon the sides of the flask whenever the temperature was allowed to rise much above that required for the fusion of the chloride. For this reason no more heat was applied than was necessary to keep the contents of the flask in a liquid condition. During the cooling the flask was gently jarred in

order to facilitate the sinking of any metal which might be retained by the chloride.

The solidified material had a grayish white color, and a cleavage resembling that of talc or brucite. Under the microscope it appeared to be homogeneous and free from metal. It also gave no metallic streak when rubbed between agate surfaces. An analysis gave:

Cadmium.	Chlorine.
64.27 per cent.	35.61 per cent.

These proportions are nearly those of a compound having the composition Cd_2Cl_7 , in which the calculated percentages are:

Cadmium.	Chlorine.
64.34	35.65

In order to determine whether this close approximation to definite atomic proportions might not be accidental, we reheated the material with an excess of the metal for twenty hours. An analysis of the product gave:

Cadmium.	Chlorine.
64.33 per cent.	35.75 per cent.

Two other portions of the substance were then prepared from fresh materials. On analysis, the first gave:

Cadmium.	Chlorine.
64.30 per cent.	35.61 per cent.
64.35	35.66

the second:

Cadmium.	Chlorine.
64.42 per cent.	35.74 per cent.

When the new substance is heated it fuses to a red liquid, and then breaks up into metal and the chloride of cadmium. Its reactions are, in general, those of a strong reducing agent. Treated with nitric acid it yields oxides of nitrogen. With dilute hydrochloric, sulphuric and acetic acids it gives free hydrogen. In the presence of dilute acids it reduces mercuric to mercurous chloride or to metallic mercury.

Three determinations of its reducing power were made, with portions of different preparations, by dissolving in hydrochloric acid and exploding the hydrogen which was evolved with air. The following results were obtained:

Hydrogen found,	Hydrogen calculated for Cd_4Cl_7 ,
15.67 cc.	15.65 cc.
11.80	11.82
23.00	23.03

Notwithstanding the fact that the cadmium and chlorine are present in atomic proportions which remain constant however long the chloride is heated with an excess of the metal, and the fact that the material appears to be homogeneous, it is by no means clear that the substance is a definite chemical compound. It appears to us quite as probable that, in the molten condition, it is a solution of a cadmous chloride in the ordinary chloride of cadmium, or possibly a double compound of the two; and that the cadmous compound cannot accumulate beyond a certain limit, owing to the ease with which it breaks up into metal and the original chloride. This view as to its composition is somewhat strengthened by the fact that when the substance is treated with water it yields the chloride and a cadmous hydroxide of normal composition, CdOH .

The anhydrous bromide of cadmium was prepared by dissolving the carbonate in aqueous hydrobromic acid, evaporating to dryness with an excess of the acid, and heating the residue in a current of dry hydrobromic acid gas. When the bromide was heated with the metal in an atmosphere of nitrogen, it behaved in all respects like the chloride under the same conditions. The fused material quickly assumed a deep red color. On being more highly heated it gave up metal which collected in globules or in a thin film upon the sides of the flask. On cooling it solidified to a grayish white mass which resembled in crystalline structure the product which was obtained by a similar treatment of the chloride. This, also, appeared to be free from metal, and homogeneous. The substance was found to contain cadmium and bromine in the proportions represented by the formula Cd_4Br_7 . Two analyses gave:

Cadmium.	Bromine.
44.59 per cent.	55.46 per cent.
44.57	55.47

The calculated percentages for Cd_4Br_7 are:

Cadmium.	Bromine.
44.45	55.55

As in the case of the chloride, it was found that reheating with the metal did not appreciably change the proportions of the constituents.

The substance is a strong reducing agent: giving with nitric acid, oxides of nitrogen; with dilute hydrochloric, sulphuric or acetic acid, free hydrogen; and with mercuric chloride, mercurous chloride or metallic mercury. Treated with water, it yielded the bromide of cadmium and cadmous hydroxide, CdOH .

The iodide of cadmium was prepared in the same manner as the bromide. Heated with the metal in an atmosphere of nitrogen, it acquired a deep red color. On cooling, the solidified material presented an appearance like that of the products obtained from the chloride and bromide. Owing to the high specific gravity of the iodine compound, some difficulty was experienced in obtaining a preparation free from metal. But this difficulty was finally overcome by keeping the material for a long time just above its melting temperature and constantly jarring the flask. Two determinations of cadmium in the first satisfactory preparation gave 31.43 and 31.51 per cent. of the metal. As these results did not correspond to a composition represented by the formula Cd_2I_7 , which our experience with the chloride and bromide had led us to expect, we reheated the material for several hours with the metal. But two analyses of the last product gave:

Cadmium.	Iodine.
31.44 per cent.	68.65 per cent.
31.39	68.68

showing that the iodide had absorbed during the first heating all of the metal which it was capable of retaining. The analytical results suggest the formula $\text{Cd}_{12}\text{I}_{23}$ or $\text{CdI} + 11\text{CdI}_2$, in which the calculated percentages are:

Cadmium.	Iodine.
31.53	68.47

In its conduct towards dilute hydrochloric and acetic acids and water, the substance behaves like the products obtained from the chloride and bromide.

When the substances just described are treated with water they yield the ordinary halogen salts of cadmium which dissolve; a small quantity of hydroxide which renders the water turbid;

and heavy, transparent, highly lustrous, crystalline substances, which quickly lose their crystalline appearance and pass over into a grayish white amorphous compound, which we have found to be normal cadmous hydroxide, CdOH . All attempts to determine the composition of these intermediate crystalline compounds have failed, owing to the rapidity with which, in the presence of water, they are converted into hydroxide. Even with the most rapid work they could not be isolated in an undecomposed condition.

Analyses of the partially decomposed materials gave quite variable proportions of metal and halogen, but never less than eight equivalents of the former to one of the latter. The production of cadmic hydroxide is evidently an essential part of the decomposition by water; since the substances, before the treatment with water, were free from oxygen, as we assured ourselves by repeated analyses. But we are not able, as yet, to explain its origin.

Notwithstanding the rapidity with which the decomposition of the crystalline compounds begins, long continued washing is necessary in order completely to remove the halogen. The extraction of the last traces of chlorine, bromine or iodine is hastened by the use of warm instead of cold water. But the temperature must not exceed 50°C . In water whose temperature approaches the boiling point, the hydroxide is slowly decomposed with separation of metal.

The new hydroxide is a strong reducing agent. It dissolves in dilute acids; yielding with nitric acid oxides of nitrogen, with other acids free hydrogen. The material which was examined more particularly by us was derived from the chloride. After washing with slightly warmed water until the last traces of chlorine had disappeared, it was dried over phosphorus pentoxide and analyzed. The results were:

Cadmium.	Water.
86.93 per cent.	7.06 per cent.
86.91	

The calculated percentages for CdOH are:

Cadmium.	Water.
86.80	7.00

The determination of the water was made by placing a small tube containing the material in a larger and longer one and

heating in a bath of sulphuric acid. During the heating a slow current of dry nitrogen was passed over the substance.

When the temperature at which the sulphuric acid gives off dense white clouds is reached, the hydroxide gives up all of its water and passes over into a heavy yellow powder. Under the microscope this powder was found to consist of minute translucent crystals. Analyses of two specimens gave 93.14 and 93.17 per cent. of cadmium. The calculated percentage of metal in Cd_2O is 93.33. If water of too high temperature is employed in washing the hydroxide, the suboxide has a greenish tint, and the presence of free metal in it may be detected under the microscope and by rubbing between agate surfaces. If the yellow suboxide is strongly heated it breaks up into a mixture of oxide and metal which possesses a distinctly green color. A supposed suboxide of cadmium has been described by R. Marchand¹ as a green substance which can be obtained by heating the oxalate to the temperature of melting lead. But the product of such a decomposition of the oxalate was found by Vogel² to consist of a mixture of oxide and metal.

Towards acids the suboxide conducts itself like the subhydroxide.

It is a fact of some interest in connection with the periodic arrangement of the elements, that the tendency toward the formation of a lower series of compounds, which becomes so strongly developed in mercury, begins to exhibit itself in some slight degree in cadmium.

ON SILVER FORMANILIDE.

BY W. J. COMSTOCK AND FELIX KLEEBOEG.

That acid anilides can form salts with metals was first shown by Hofmann³ in 1865, when he succeeded in preparing the sodium salt of formanilide. Salts of acid amides with the heavy metals had been prepared previously, and since that time numerous investigators have had occasion to work with similar compounds.

¹ Pogg. Ann. 38, 143.

² Jahresbericht 1855, 390.

³ Berl. Akad. Ber. 1865, 659.

Bunge¹ first prepared sodium acetanilide by acting with metallic sodium on the hot solution of acetanilide in xylene, and in the same paper states that he was unable to prepare silver salts of either formyl- or acetanilide. Hepp's well known synthesis of mono-methyl-aniline from sodium acetanilide shows that the structure of this salt is $\text{C}_6\text{H}_5\text{N} \begin{smallmatrix} \text{Na} \\ \text{COCH}_3 \end{smallmatrix}$.

Although Tobias² was unable to obtain methyl-formanilide from sodium formanilide, it has since been shown by Norton and Livermore,³ as well as by Pictet and Crépieux,⁴ that this synthesis is possible, so that in this latter salt as well sodium is united with the nitrogen. In the group of analogous thio-anilides, which differ from the ordinary acid anilides in that they are readily soluble in cold dilute alkalies, another structure must be assumed for the sodium salts. Wallach⁵ showed that the sodium salt of thiaceetanilide does not give the normal ethyl-thiaceetanilide,

$\text{C}_6\text{H}_5\text{N} \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{CSCH}_3 \end{smallmatrix}$ by treatment with ethyl bromide, but that an isomeric compound, $\text{C}_6\text{H}_5\text{N}=\text{C} \begin{smallmatrix} \text{SC}_2\text{H}_5 \\ \text{CH}_3 \end{smallmatrix}$, which he called ethyl-iso-thiaceetanilide, is formed. Since then the investigation of similar thio-anilides has led to the conclusion that in the sodium salts of bodies of this class, the metal is united with sulphur rather than with nitrogen.

Notwithstanding the failure of Bunge to obtain a silver salt of formanilide, it can be prepared in quantity with no more inconvenience than attends the preparation of other amorphous silver salts that are sensitive to light.

An investigation of this salt has led us to the interesting result that, although in sodium formanilide the metal is, as mentioned above, united with nitrogen, to the silver salt must be assigned the structure $\text{C}_6\text{H}_5\text{N}:\text{C} \begin{smallmatrix} \text{OAg} \\ \text{H} \end{smallmatrix}$. If silver formanilide and methyl iodide are allowed to react in molecular proportions, silver iodide is formed together with a compound, the analysis of which gave results agreeing with formyl-mono-methyl-aniline, but whose properties and decompositions are entirely different. The boiling point and the characteristic odor show at once that the body is

¹ Ann. Chem. (Liebig), Suppl. 7, 122.

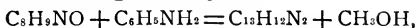
² Ber. d. chem. Gesell. 15, 2452.

³ Ibid. 20, 2273.

⁴ Ibid. 21, 1106.

⁵ Ibid. 11, 1590.

not formyl-mono-methyl-aniline. With aniline the new compound reacts according to the equation



and the compound, $\text{C}_{13}\text{H}_{12}\text{N}_2$, is the well known diphenyl-form-

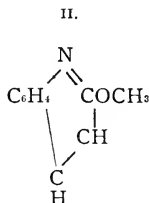
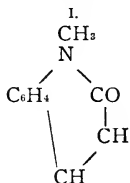
amidine, $\text{CH} \begin{array}{l} \text{NHC}_6\text{H}_5 \\ \text{=NC}_6\text{H}_5 \end{array}$, the structure of which can be regarded

as settled. This reaction and the formation of the new compound from silver formanilide show beyond doubt that its structure is $\text{C}_6\text{H}_5\text{N}=\text{C} \begin{array}{l} \text{OCH}_3 \\ \text{<H} \end{array}$; we shall speak of it hereafter as methyl-isofromanilide, in conformity with the nomenclature adopted by Wallach for the corresponding thio-compounds, or as phenyl-form-imido-methyl ether, on account of its analogy to the imido ethers of Pinner. Below are given the details of the reaction. It is our intention to give a more complete study of this class of compounds at a future date, the object of this paper being to call attention to the behavior of silver formanilide, and the connection of our results with the question of the constitution of compounds containing the group $\text{NH}-\text{CO} \begin{array}{l} | \\ | \end{array}$, or $\text{N}=\text{C.OH} \begin{array}{l} | \\ | \end{array}$.

Compounds of this nature received a great deal of attention during the few years succeeding the publication by Baeyer and Oekonomedes¹ of their work on isatine. Essentially the same question had previously come up regarding cyanic and cyanuric acids, and the method of attacking the problem was the same, *i. e.* to study the ethers. If the ether contained the alkyl group attached to oxygen, it was regarded as proof that the original compound contained the group $\text{N}=\text{C.OH} \begin{array}{l} | \\ | \end{array}$, while the other arrangement of atoms (now frequently spoken of as the tautomeric form) was assumed when the ether contained the alkyl attached to nitrogen. This led to the adoption of formulæ containing the two different groups for compounds in which the same arrangement might well have been expected. For example, isatine was a lactim having the group $\text{N}=\text{COH} \begin{array}{l} | \\ | \end{array}$, and oxindol was a lactam with the group $\text{HN}-\text{CO} \begin{array}{l} | \\ | \end{array}$; carbostyryl was a lactim, while oxy-pyridine and hydrocarbostyryl were lactams. In preparing the

¹ Ber. d. chem. Gesell. 15, 2093.

ethers the silver salts were sometimes used; frequently the alkyl halide was made to act on the sodium or potassium salt in alcoholic solution. It was supposed that the result would be the same whichever of these two methods was used. Friedländer,¹ in collaboration with Weinberg and afterwards with Müller, showed that, according to the method adopted, the lactam-ether (Fig. I) or the lactim-ether (Fig. II) could be prepared from carbostyryl.



Friedländer suggested that other compounds may show a similar behavior. In looking over the literature up to that date, it is interesting and suggestive to see how the conclusions as to the structure of these compounds depended entirely on the method used in preparing the ethers. Isatine,² isatoxime,³ and carbostyryl were lactims; their ethers were prepared from the silver salts. γ -Oxyquinaldine,⁴ oxynicotinic acid,⁵ pseudo-lutidostyryl⁶ and oxindol⁷ all gave ethers in which the alkyl group was joined to nitrogen; their ethers were prepared by the action of the alkyl halide and sodium alcoholate or an alcoholic solution of potassium hydroxide. It is especially interesting that ethyl-pseudoisatine- α -ethoxim,⁸ from which Baeyer made ethyl-pseudoisatine,

$\text{C}_6\text{H}_4 \begin{array}{l} \text{NC}_2\text{H}_5 \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{CO}$, was prepared with sodium alcoholate and ethyl iodide.

In this connection an experiment which we recently made is worth mentioning, though only indirectly bearing on the rest of this paper. Isatine was boiled in alcoholic solution with ethyl iodide and the theoretical quantity of sodium alcoholate for two hours. On boiling off the greater part of the alcohol and adding water, a dark resinous product separated; this product gave, after shaking out

¹ Ber. d. chem. Gesell. **18**, 1528, and **20**, 2009.

² Baeyer and Oekonomides: *Ibid.* **15**, 2093.

³ Baeyer and Comstock: *Ibid.* **16**, 1704.

⁴ Knorr and Antrick: *Ibid.* **17**, 2870.

⁵ v. Pechmann: *Ibid.* **18**, 317, and **17**, 2390.

⁶ Hantzsch: *Ibid.* **17**, 2903.

⁷ *Ibid.* **16**, 1704.

⁸ Baeyer: *Ibid.* **16**, 2188.

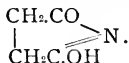
with ether and evaporating the ether, a well crystallised body, but mixed with a considerable quantity of the resinous material. It was, however, easily purified by crystallising from boiling water. After a second recrystallisation it fused at 95° . The compound corresponds exactly to the description of ethyl-pseudo-isatine. It dissolves in dilute potassium hydroxide, giving a light yellow solution, from which it is precipitated at once unaltered on

the addition of an acid. The compound, $\text{C}_6\text{H}_5 \begin{array}{c} \diagup \text{N} = \\ \diagdown \text{CO} \end{array} \text{COC}_2\text{H}_5$,

corresponding to the methyl ether obtained by Baeyer and Oekonomedes from the silver salt of isatine, should regenerate isatine under these conditions. We have no intention of entering into a discussion of the "tautomerism" of the groups $\text{CO} - \text{NH}$, $\text{HO.C} = \text{N}$, but would call attention to the fact that it is the tendency of a silver atom entering into such a compound to give it the form $\text{C.OH} = \text{N}$, even where the alkali salts are derived from the lactam form $\text{CO} - \text{NH}$.

One compound in which the group $\text{CO} - \text{NAg}$ has been hitherto regarded as existing beyond question, has interested us on account of the iodine compound made from it: silver succinimide. We shall describe later on the action of iodine on silver formanilide, and the formation of the compound $\text{C}_7\text{H}_6\text{NOI}$, whose only analogue known thus far (at least as far as its formation is concerned) seems to be Bunge's¹ "iodo-succinimide," prepared by acting with iodine on silver succinimide. The formation of the compound $\text{C}_7\text{H}_6\text{NOI}$ at ordinary temperature from silver formanilide makes it probable

that the compound has the structure $\text{C}_6\text{H}_5\text{N} = \text{C} \begin{array}{c} \text{H} \\ \diagdown \text{OI} \end{array}$. The formation of iodo-succinimide under the same conditions led us to the idea that both iodo- and silver succinimide might be derivatives of the form



The experimental verification of this did not, however, work as smoothly as we had hoped. The results will be published at a later date.

Silver formanilide.—This salt can be prepared by dissolving the sodium salt in alcohol of about 50 per cent., and gradually adding the theoretical quantity of silver nitrate, also in dilute

¹Ann. Chem. (Liebig), Suppl. 7, 119.

alcoholic solution, stirring the solution well meanwhile. After the silver nitrate solution is all added it is advantageous to add more water and wash partly by decantation. The salt is white when first precipitated, but by the time it has been washed and dried it always has a gray color, light or dark according to the time used and its exposure to light. It is amorphous. A quicker method of preparing it is to dissolve the theoretical quantities of formanilide and silver nitrate in dilute alcohol, adding gradually the theoretical quantity of pure sodium hydroxide with constant stirring, and washing with water as in the other method. At ordinary temperature the salt is quite stable. Unless great care is used to avoid an excess of the alkali and to use pure alkali, the purity of the salt suffers.

A silver determination gave $\text{Ag} = 47.89$ per cent.; calculated for $\text{C}_6\text{H}_5\text{N}=\text{C} \begin{smallmatrix} \text{O} \\ \text{H} \end{smallmatrix} \text{Ag}$, $\text{Ag} = 47.37$ per cent.

Methyl-iso-formanilide.—When silver formanilide is treated with methyl iodide in molecular proportion, the iodide being diluted with a small quantity of perfectly dry ether, a thick paste is formed, or indeed, where the quantity of ether used is small, the liquid is entirely absorbed by a part of the salt while the rest looks perfectly dry. On standing for a time at ordinary temperature the appearance of the mixture gradually changes; it becomes more fluid, and after 24 hours the formation of silver iodide seems to be complete. When large quantities are used the reaction is accompanied by evolution of heat, sufficient to make the ether boil. More ether is now added and the liquid filtered from silver iodide. After boiling off the ether a heavy oil is obtained, the greater part of which boils from 195° – 200° , and on redistilling, a colorless product, boiling at 196° – 198° , results.

Analysis showed the composition $\text{C}_8\text{H}_9\text{NO}$.

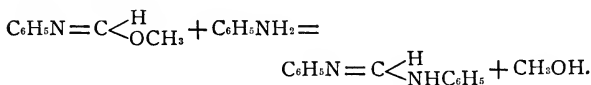
	$\text{C}_8\text{H}_9\text{NO}$, calculated,	Found,
C	71.11	71.39
H	6.66	6.89
N	10.37	10.41

As to the structure of this compound there can be no question; it is represented by the formula $\text{C}_6\text{H}_5\text{N}=\text{C} \begin{smallmatrix} \text{H} \\ \text{OCH}_3 \end{smallmatrix}$.

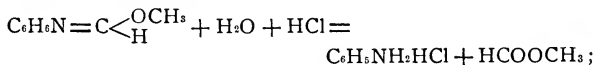
The tendency of methyl-iso-formanilide to form diphenyl formamidine is marked; it is analogous to the behavior of the imido-

ethers and the iso-thio-anilides. When mixed with aniline in molecular proportion the mixture warms up and finally becomes solid. The amidine was purified by recrystallisation from alcohol.

The reaction is



The same reaction takes place when aniline is added to methyl-iso-formanilide in the presence of a large quantity of water. A dilute solution of aniline hydrochloride converts it at once into the hydrochloric acid salt of diphenyl-formamidine. For the preparation of the amidine the addition of aniline is not necessary. If hydrochloric acid, strong or dilute, is added to methyl-iso-formanilide, diphenyl-formamidine hydrochloride is formed at once. This is easily understood in the light of the former reactions. The reaction takes place in two phases. The first change is represented by the equation,



and, second, the aniline hydrochloride formed acts at once on unaltered methyl-iso-formanilide. In the first phase the reaction is exactly analogous to the behavior of benzylidene-aniline, $\text{C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_5$, on treatment with acids. The formation of the amidine also takes place, though slowly, on exposing the iso-formanilide to moist air. In all cases the diphenyl-formamidine melted at 137° – 138° after recrystallising from alcohol.

	$\text{C}_{13}\text{H}_{12}\text{N}_2$ calculated.	Found.
C	79.60	79.82
H	6.12	6.15
N	14.28	13.94

Analysis, a comparison of the compound with diphenyl-formamidine prepared by other methods, and the splitting off of aniline¹ by boiling with dilute alcohol, serve to establish the identity of the compound beyond question.

Action of iodine on silver formanilide.—When the finely pulverised silver salt is mixed with dry chloroform and one molecule iodine is added, the formation of silver iodide begins at once. If

¹ Ber. d. chem. Ges. 15, 2450.

the iodine is dissolved in chloroform before it is added, the reaction takes place rapidly at ordinary temperature; but no harm is done by warming on the water-bath. In taking molecule for molecule of the silver salt and iodine, the chloroform solution retains the iodine color, but on adding an excess of silver salt it is colored amber-yellow. After filtering from the silver iodide the solution is concentrated, first on the water-bath, finally at ordinary temperature, by passing a current of dry air over it until quite a quantity of light yellow crystals has separated. These are washed with dry ether to free them from the mother-liquor and from a small quantity of reddish oil. The new compound can be recrystallised from ether or chloroform, but unless great care is taken to work quickly and avoid moisture there is a separation of iodine. Dry ether or pure acetone can be used in place of chloroform in making the reaction, but we obtained a better yield in using chloroform and working with small quantities. The best yield was 2.7 grams from 5 grams silver salt. On heating the compound decomposes with separation of iodine; the separation is less, the more slowly it is heated. After keeping for a time it also smells strongly of iodine, and iodine crystals can be observed. An iodine estimation gave 50.27 per cent. iodine. The theory for C_7H_6NOI requires 51.42 per cent. iodine. The iodine determination shows clearly that the compound is derived from silver formanilide, by the introduction of one atom of iodine in the place of silver. Bunge has shown that iodine does not react with sodium formanilide, in which the metal is united with nitrogen.

We have shown that in silver formanilide the metal is attached to oxygen. The ready formation of the new compound from silver formanilide at ordinary temperature, together with Bunge's observation, seem to warrant our conclusion that its structure is represented by the formula $C_6H_5N=C\begin{smallmatrix} H \\ \diagdown \\ OI \end{smallmatrix}$. Perhaps the best name that can be given to it is iodo-iso-formanilide. Iodo-iso-formanilide is decomposed by water, but we have not attempted to study the products. No definite melting point can be given. When slowly heated the separation of iodine is not large, and the contents of the tube are melted at about 110° , but in this case a second compound, the result of molecular rearrangement, is formed.

Para-iodo-formanilide.—After heating iodo-iso-formanilide slowly and keeping the temperature for a few minutes at 115° ,

then crystallising from water, we obtained this second body in fine white transparent needles melting at 109° – 110° . An iodine estimation gave 51.13 per cent. iodine.

The theory for C_6H_5NOI requires 51.42 per cent. This same rearrangement can be effected by heating iodo-iso-formanilide for a few minutes with formic acid; indeed, on adding formic acid it dissolves, heat is evolved, and the new compound needs only to be crystallised from water. The new body is para-iodo-formanilide. To prove its identity we prepared para-iodo-aniline by the method described by Michael and Norton,¹ and made the formyl compound. By boiling *p*-iodo-aniline with a slight excess of formic acid for a few minutes, boiling off the excess of acid and crystallising from hot water, we obtained the formyl compound in long needles exactly like those obtained from iodo-iso-formanilide.

	Calculated for $C_6H_4I.NHCHO$.	Found,
Iodine	51.42	51.77

It dissolves easily in alcohol, methyl alcohol acetone, ether, chloroform and benzene, with difficulty in cold water, more readily in hot water. The melting point remained constant after repeated recrystallisations from water at 108° – 109° .

This formation of para-iodo-formanilide from iodo-iso-formanilide suggests the reaction which Bender described.² From a compound whose structure Bender considered to be $C_6H_5N \begin{smallmatrix} \text{Cl} \\ \diagup \\ \text{COCH}_3 \end{smallmatrix}$, he obtained by molecular rearrangement *p*-chlor-acetanilide.

Our conclusion as to the structure of iodo-iso-formanilide suggested a re-examination of a number of compounds in which it has been supposed that the halogen is united to nitrogen. The work is now under way in this laboratory, and the results will be communicated later.

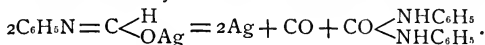
Formation of carbanilide.—On dry distillation of silver formanilide a solid crystallised compound is formed. This is easily separated from the oily products by washing with alcohol, and can be obtained pure by recrystallising from alcohol. It turned out to be *s*-diphenyl-urea.

	$CO(NHC_6H_5)_2$.	Found,
C	73.59	73.32
H	5.66	6.00
N	13.20	13.43

¹ Ber. d. chem. Gesell. 11, 108.

² Ibid. 19, 2273.

It fused at 231° – 233° , corresponding exactly to a specimen of diphenyl-urea prepared according to Weith.¹ We also converted some of the diphenyl-urea, obtained from silver formanilide, into triphenyl-guanidine, which melted at 144° , so that its identity is certain. The reaction by which it is formed can be formulated:



That carbon monoxide is formed we proved in the customary way. The formation of disubstituted ureas from silver salts of the formyl compounds seems to be general. On distilling silver form-para-toluide, and recrystallising the product from alcohol, we obtained dipara-tolyl-urea melting at 255° .

Calculated for $\text{CO}\begin{smallmatrix} \text{NHC}_6\text{H}_4\text{CH}_3 \\ \text{NHC}_6\text{H}_4\text{CH}_3 \end{smallmatrix}$.		Found.
C	75.00	74.77
H	6.67	6.77
N	11.66	11.63

SHEFFIELD LABORATORY, NEW HAVEN.

DICHLOR-SALICYLIC ACID.

BY JOSEPH L. HECHT.

The literature upon this subject furnishes us with descriptions of four acids, supposed to differ in chemical and physical properties, which means, necessarily, a difference in constitution.

First, Cahours, as early as 1845,² called attention to a dichlor-salicylic acid, obtained by the chlorination of potassium salicylate. His description of the properties of the acid and salts is so meagre that little importance can be attached to this publication.

Second, Rogers in an inaugural dissertation (Goettingen, 1875) mentioned an acid similar in composition, obtained by conducting a calculated amount of chlorine into glacial acetic acid containing dissolved salicylic acid. The acid thus obtained melted, according to Rogers, at 224° C., and gave a barium salt containing five molecules of water.

Third, Smith³ obtained a dichlor acid by chlorinating salicylic

¹ Ber. d. chem. Gesell. **9**, 821.

² Ann. Chem. (Liebig) **52**, 340.

³ Proc. Am. Phil. Soc., June 15, 1877, p. 69; also Ber. d. chem. Gesell. **11**, 1225.

acid dissolved in ethyl alcohol. It melted at 214° C., and gave a barium salt containing three and one-half molecules of water of crystallisation.

Fourth, William Pauli in an inaugural dissertation (Goettingen, 1878) described a dichlor-salicylic acid produced by conducting a calculated amount of chlorine through carbon disulphide containing a weighed amount of salicylic acid in suspension. He gave as the melting point 223° – 225° C., and stated that it forms a barium salt containing six molecules of water.

Dr. Smith having had occasion to prepare dichlor-salicylic acid according to the method described by Rogers, found that it was identical with the acid prepared by chlorination of salicylic acid in alcohol. This having occurred, the question arose, do the differences claimed for these acids really exist? The matter was handed to me at this stage. It was evident that in three of the four cases the only difference in preparation was the solvent used; in the other case the salt was first formed and the chlorine then introduced. Therefore, in the three cases above referred to, if there is a difference, it must be due to the solvent; in the other case a difference must be caused by the influence which the presence of potassium in the molecule might have on the entering chlorine atoms. Would the solvents in the one case and the presence of potassium in the other so influence the substitution as to produce different dichlor acids? Taking this as the first step towards the solution of the problem, I proceeded in the following manner. First, the fact that the acid of Rogers had been prepared and thoroughly studied by Dr. Smith, and by him shown to be identical with the acid chlorinated in alcohol, made it unnecessary for me to repeat that work, the details of which are given in the articles cited above. The acid of Pauli, who gave as its melting point 223° – 225° C., was made as described by him, viz. by conducting a calculated amount of chlorine into carbon disulphide containing salicylic acid in suspension. A solution of caustic potash was then added and the potassium salt thus formed. As this is much more easily soluble than the acid it can be easily separated from the oily liquid. This was done by means of a separatory funnel. The potassium salt was then decomposed by hydrochloric acid. The acid thus liberated, after filtration and washing, was boiled with an excess of barium carbonate, producing the barium salt. The chlorination produced both monochlor and dichlor-salicylic acids; hence I found mixed with the

barium dichlor-salicylate barium mono-chlor-salicylate, but was able to separate the two salts by fractional crystallisation, the barium dichlor salt being the more insoluble, and by repeated crystallisation it was obtained pure. This crystallised in large, almost colorless needles.

While this salt was being prepared I made the dichlor acid and barium salt according to the method of Smith, viz. by chlorination of salicylic acid in alcohol. The alcoholic solution of the acid thus formed was thrown into a large quantity of water, which caused the separation of the acid. After filtering and washing, the barium salt was formed and purified as in the preceding case. During the entire operation the salts of the two acids appeared to be identical. Samples of each were taken, and after drying in the air-bath were weighed and analysed with the following results: Of the air-dried salt prepared by Smith's method 0.2867 gram was taken; the loss on drying at 170° C. until constant weight resulted was 0.0330 gram = 11.51 per cent. H_2O . The anhydrous salt gave 0.1064 gram $BaSO_4$ = 0.0626 Ba = 21.84 per cent. Ba. Of the air-dried salt prepared by Pauli's method, 0.4127 gram lost on drying at 170° C. until constant weight was obtained 0.0468 gram = 11.34 per cent. H_2O , and gave $BaSO_4$, remaining after evaporation with H_2SO_4 , 0.1542 gram $BaSO_4$ = 0.0906 Ba = 21.95 per cent. Ba. The theoretical percentages of barium and water required by a salt of the following composition, $(C_6H_2Cl_2OHCOO)_2Ba + 4H_2O$, are 22.06 per cent. Ba and 11.59 per cent. H_2O . Smith found three and one-half molecules of water, but on reference to his paper I find he dried the salt over calcium chloride previous to heating in air-bath. I may mention here, in the determination of water great care is necessary that the temperature does not exceed 170° C., otherwise an aromatic odor is developed which undoubtedly indicates a slight decomposition, and the loss in weight calculated as water is consequently erroneous. From the pure salts the acids were liberated and were repeatedly crystallised from a mixture of alcohol and water, from which they separated in the form of white arborescent needles. Portions of the crystallised acids were melted side by side and showed a constant fusing point of 214° C. Samples of each were also sublimed between watch-glasses, and the sublimate thus obtained melted likewise at 214° C. That no doubt might remain as to these being dichlor acids, a determination of the chlorine was carried out. Of the acid prepared by Smith's

method, 0.2210 gram burned with calcium oxide gave 0.3083 gram $\text{AgCl} = 0.07619$ gram $\text{Cl} = 34.47$ per cent. Cl .

Of the acid prepared by Pauli's method 0.2120 gram gave 0.2930 gram $\text{AgCl} = 0.07255$ gram $\text{Cl} = 34.12$ per cent. Cl . The theoretical amount of chlorine required by dichlor-salicylic acid is 34.25 per cent.

The acid of Cahours was next prepared. Potassium salicylate was made by treating a boiling solution of salicylic acid with potassium carbonate. The salt thus obtained was purified by crystallisation, after which it was dissolved in water and chlorine conducted through the solution until the precipitate ceased to form. This precipitate was potassium dichlor-salicylate. It was filtered and washed, then brought into solution by boiling water and the acid liberated with hydrochloric acid; after filtration it was boiled with barium carbonate. Through the barium salt thus formed I was enabled to obtain the acid in a pure state. I may also mention that I obtained here a barium salt of the mono-chlor acid, from which the dichlor salt was separated by fractional crystallisation, as in the preceding cases. In fact, all that was observed in connection with the salts of the acids prepared by the other methods was here also observed. From this salt the acid was set free by hydrochloric acid and recrystallised several times from a mixture of alcohol and water. On comparing the behavior of this acid with that of those prepared by the other methods, the same statement holds good that was made in comparing the salts of this acid with those of the acids prepared by the other methods. The acid of Cahours melted sharply at 214°C .

Later, I distilled samples of the acids mixed with calcium oxide and sand in the proportion of one part acid to three parts calcium oxide. The heat was so regulated that the mixture merely browned in spots. In the case of each distillation an oily liquid came over, which upon a reduction of temperature solidified to colorless needles. These needles melted at 43°C . and gave out the characteristic odor of dichlor-phenol of the constitution

$\text{C}_6\text{H}_3 \begin{cases} \text{OH} & (1) \\ \text{Cl} & (2) \\ \text{Cl} & (4) \end{cases}$. It is evident that to produce this compound the

original acids must have had the constitution represented by the
formula $\text{C}_6\text{H}_2 \begin{cases} \text{COOH} & (1) \\ \text{OH} & (2) \\ \text{Cl} & (3) \\ \text{Cl} & (5) \end{cases}$.

Thus there no longer remains a doubt as to the positions of the chlorine atoms in the dichlor acids; they have the same constitution and are identical. I may also add that Lössner¹ found that when antimony pentachloride acted upon salicylic acid, a dichlor acid was formed which melted at 214° C. From the facts herein given I feel justified in concluding that at present we have *but one dichlor-salicylic acid*, the structural constitution of which is represented above. Its melting point is 214° C.

The above work was carried out under the direction of Dr. Smith, and it is to him I owe, in great measure, my success in arriving at the above conclusion.

UNIVERSITY OF PENNSYLVANIA.

REVIEWS AND REPORTS.

THE ELECTROLYTIC DISSOCIATION.—HYPOTHESIS OF SVANTE ARRHENIUS.

In 1857, almost simultaneously, Williamson and Clausius put forward the hypothesis that, in the fluid state at least, the molecules of compounds are not stable, in the sense that they are persisting aggregations of the identical molecules which originally united to form them; on the contrary, it was assumed that these molecules in so far resemble living organisms that, while the external appearance remains unchanged, the constituents are constantly being cast off and replaced by new ones of the same kind, so that there must always be a few molecules in a state of *dissociation*. This hypothesis has been favorably regarded as an explanation of the possibility of the coexistence of two opposing reactions, like those of etherification and saponification, where it is left to the chance encounter of molecules to occasion the existence of water and ether, or of alcohol and acid; it has likewise been regarded as a plausible explanation of the readiness with which an electrolyte will obey the influence of currents so feeble that their energy should not suffice to decompose a single molecule whose atoms were held together by their full chemical attraction. But when, six years ago, the attempt was made by Arrhenius to give a quantitative expression to this hypothesis, and to apply it to the explanation of all the anomalies observed in the physical

¹ J. prakt. Chem. 13, 431.

behavior of solutions, much latent hostility was called forth, and a general discussion was aroused, which has continued until the present time. It appears, however, to the reviewer that a point has now been reached where the burden of proof would rest upon the opponents rather than upon the supporters of the hypothesis. An analysis of this discussion, set forth in proper order, might prove both lengthy and confusing, and I therefore relegate a chronological list of the original papers to the end of this review and confine myself to a brief exposition of the hypothesis as it stands at present, and of the chief objections which have been raised to it.

The fundamental idea is this: In electrical conductors of the second class electricity can be *transported* only by electrically "active" molecules, *i. e.* those in which the electrostatic charges are not neutralised within the molecule; the *ions* are able to receive and transport charges, positive and negative respectively, as long as they are separated, but not when they are firmly knit into a neutral molecule. It follows that there can be no conduction without a pre-existent partial dissociation of the molecules, which may be occasioned either by heat or more generally by the presence of a foreign body, such as water. It is, for instance, a well known fact that some of the best conductors, like the strong acids, become insulators when freed from the last traces of water, while water itself is classed among the poorest conductors when free from impurities. The mechanism by which water, *par excellence*, should produce electrolytic dissociation, while alcohol and other solvents do not, has yet to be explained; it does seem strange that such an effect should be produced without a corresponding dissociation of the water, an idea which Arrhenius rejects or admits only to a minimal extent. However that may be, electrolytic dissociation is assumed to be a phenomenon precisely corresponding to gaseous dissociation and obedient to laws expressed by the same thermodynamic formulæ, with this difference, that "osmotic" pressure must replace gas pressure. Consequently, dissociation must be increased by dilution (increase of volume) and by heat; but for different substances the corresponding coefficients may differ.

1. The first application of this hypothesis affects Kohlrausch's law of conduction; the conducting power of an electrolyte is no longer the sum of the velocities of all the ions, but of that proportion which are free to move. Only for extreme dilutions do we find a rigorous adherence to the equation $\lambda = u + v$, which becomes in less dilute solutions $\lambda = \alpha (u + v)$ (I), where α expresses the "coefficient of activity," or that proportion of the whole number of molecules which is dissociated. Experiments having given very reliable results for u and v in the case of quite a number of ions, and λ being known for a large number of compounds, at

¹ Compare this Journal 11, 116.

various degrees of concentration, the respective values of α are readily obtained.

2. The number of molecules in the solution is increased by the dissociation. If each molecule is dissociated into k constituent ions, and n_1 molecules are thus broken up, while n remain associated, the osmotic pressure must correspond to the presence of $n + kn_1$ molecules, instead of $n + n_1$. We shall have for the relation of the true osmotic pressure to that calculated upon the assumption that the molecules remain intact, $i = \frac{n + kn_1}{n + n_1}$.

The definition of the coefficient of activity has introduced the value $\alpha = \frac{n_1}{n + n_1}$, whence

$$i = 1 + (k - 1)\alpha \quad (\text{II}).$$

This explains the fact, alluded to in a recent review, that the molecular weight of an electrolyte, as determined by any of the "osmotic" methods, must be found smaller than theory would require. The coefficient i has been determined for many electrolytes, both by the freezing-point method and de Vries' and Hamburger's isotonomism methods, and has in almost every case been found to agree astonishingly well with the corresponding value obtained from equation II, after calculating α by equation I. The few exceptions are found for salts which behave anomalously in other respects, and can be explained by making further assumptions which need not be discussed here.

3. If $k = 2$, that is if the electrolyte consists of but two ions, as in the case of monobasic acids and their salts with monovalent metals, the dissociation ought to obey the law which has been found to hold for gaseous dissociation where one molecule breaks up into two constituents, $\frac{p}{p_1} = \text{const.}$, p now referring to the osmotic pressure of the integral molecules and p_1 to that of either set of ions of the dissociated ones. The osmotic pressure depends upon the number of molecules in the unit volume of solution. Therefore, if we call the volume of the solution V , $p = \frac{n}{V}$,

$$p_1 = \frac{n_1}{V}, \text{ and } \frac{nV}{n_1} = \text{const.}$$

If the dissociation were complete, a result reached at infinite dilution, the molecular conductivity would reach a maximum value μ_{∞} , but at the finite dilution V , it has a smaller value μ_v , which is a measure of the number of dissociated molecules in the total. We can substitute in the last equation the values $n_1 = \frac{\mu_v}{\mu_{\infty}}$, and $n = 1 - \frac{\mu_v}{\mu_{\infty}}$, and obtain

$$\frac{\mu_{\infty}(\mu_{\infty} - \mu_v)}{\mu_v} V = C.$$

In this form the ratio has been examined by Ostwald, and has been found to remain practically constant for any one substance from $\frac{1}{4}$ normal solutions up to the very highest dilutions amenable to experiment. For different acids, this constant assumes different values which have proved to be closely connected with the chemical activity of these acids. Putting $m = \frac{\mu_{\infty}}{\mu_v}$ and $K = \frac{1}{C}$, we can note for reference the equation to which Ostwald now reduces his results

$$\frac{m^2}{(1-m)V} = K. \quad (\text{III})$$

4. If the solution of an electrolyte really contains free ions, how is it that this does not at once become apparent, either by the decomposition of water, or by some physical heterogeneity of the system? The answer lies in the further definition that these free ions bear equal and opposite electrostatic charges, which do not permit any local preponderance of one sort of ions over another, as this would mean a local accumulation of electricity in a system which is in equilibrium. Consequently—although the ions travel with different velocities—if they are travelling in the same direction as in diffusion, the attraction of their electrostatic charges compels them to accommodate their rates one to another, so that the slower ion is accelerated while the faster is retarded; the rate of diffusion of the salt is therefore intermediate between the velocities of the two ions. These conditions have received a rigorous mathematical formulation, and the close agreement between the theoretical and experimental result affords a beautiful confirmation of the fundamental hypothesis. (Nernst.)

5. Any cause, on the other hand, which produces a relative dislocation of the positive and negative ions must occasion electrical heterogeneity, showing itself by differences of potential at different points. Upon this idea a plausible "osmotic" theory of voltaic electricity has been based and substantiated by experiment. (Nernst.)

6. Conversely, any difference of electrical potential in the solution must produce a motion of the ions. Here we have the Clausius hypothesis of electrolysis. The introduction of electrodes disturbs the equilibrium of the solution, the positive ion moves to the cathode, where it gives up its charge, while the negative ion does the same at the anode. It is only when the ions are relieved of their charges that they are capable of attacking the metal of the electrodes, or of decomposing water, causing the well-known secondary effects; charged, and in the paralysing presence of an opposite charge, they are supposed to be incapable of doing this. In this connection may be cited an experiment which appears incomprehensible unless free ions are assumed to exist in the solution. Dilute sulphuric acid, contained in a flask whose exterior was coated with tin-foil, was connected by a wick with a

Lippmann electrometer; upon giving a positive charge to the exterior of the flask the electrometer indicated the presence of positive electricity, and some bubbles of hydrogen were evolved near it. Consequently, the flask being a modified Leyden jar, negative ions (SO_4) had collected on the interior, while the corresponding hydrogen had been driven over toward the electrometer.

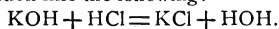
7. Properties like density, refractive power, capillarity and viscosity of saline solutions, whose numerical values appear to depend upon the sum of two factors characteristic of the acid and of the metal, should show this additive nature best where the salts are most dissociated; this appears to be the case.

8. We have now to consider the chemical side of the hypothesis, and we are met by the startling assertion that those acids show the greatest degree of dissociation which we consider the strongest. Indeed, according to Arrhenius, chemical activity depends upon the degree of electrolytic dissociation, only the dissociated molecules being capable of entering into reaction. A fundamental difference is hereby inferred to exist between reactions among electrolytes and reactions introducing only non-electrolytes, or, to recall antiquated notions, between reactions which involve substances of the water and hydrochloric acid types, and those involving merely the hydrogen and ammonia types. Valid objections raised to this distinction would upset the theory from the chemist's standpoint: examples in favor of the distinction have been adduced, such as the fact that the characteristic halogen reaction with silver nitrate is only shown by such compounds in which the halogen can be supposed to exist as a free ion, while with those which contain the halogen within the radicle, like trichloroacetic acid, the reaction fails. Considering by themselves the reactions between electrolytes, it is noticeable that the presence of water or another solvent appears to be necessary (cf. the passivity of absolutely dry gases). The law of Guldberg and Waage must be modified in so far that the speed of reaction is not a function of the total masses of the electrolytes in solution, but of the masses of dissociated ions: vant' Hoff has introduced the coefficient i (isotonic coefficient) successfully enough into these considerations, and i has already been shown to be a function of α (II). In the acceleration or retardation of etherification and saponification, the acids and bases must act proportionately to their stages of dissociation, so that Ostwald's old affinity-coefficients must correspond with the values of k in equation III, which is also found to be true; for the same reason the effectiveness of weaker acids (non-dissociated) increases more rapidly for additional dilution than does that of stronger acids which are much nearer their limit. The evidence to be obtained from the study of the kinetics of chemical reaction all appears to favor the theory.

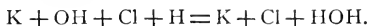
9. New ideas are introduced with regard to chemical equilibrium. The laws of dissociation, where gases are concerned, lead to the well-established postulate that dissociation shall be greatest where the atmosphere contains no excess of either of the constituents into which the molecule will break up; dissociation is unaffected by the presence of any other *indifferent* substances. By analogy, if a solution already contains a number of free ions of a particular sort, any substance consisting in part of this same sort of ions will not dissociate as fully as in pure water. Consequently an acid will be weakened by the presence of one of its neutral salts, but the effect will be much more perceptible for a weak acid than for a strong one. This has been verified by Arrhenius. Comparing, on the other hand, acids which have the positive ion H in common, a mixture of the two must affect their respective degrees of dissociation, unless before mixing the H had the same osmotic partial pressure in both solutions. This means that there shall be the same degree of dissociation in the two solutions, that they shall be "isohydric." Under such conditions, if m parts of one solution having the conductivity a be mixed with n parts of the other having the conductivity b , the resulting solution will conduct as if each electrolyte were conducting independently and unchanged. Its conductivity is $\frac{ma + nb}{m + n}$, no matter what the relative values of m and n are. Furthermore, if two solutions are "isohydric" with a third, they must be isohydrous with each other. These two consequences have been substantiated by the examination of the conductivity of mixtures of "isohydric" solutions of acids with one another and with those of their respective neutral salts, of neutral salts with one another and with the solutions of their respective bases, and finally of the bases with one another.

But if solutions are mixed together which are not "isohydric," the resultant conductivity will be greater than $\frac{ma + nb}{m + n}$, if calculation shows that the stronger acid is thereby partially reassociated and the weaker partially dissociated, while it will be less than the normal if the stronger acid is being dissociated and the weaker reassociated. This depends upon the fact that the dissociation of the same number of molecules produces a relatively greater effect when the acid is farther from the limit of dissociation which all approach asymptotically. In keeping with these facts is Nernst's observation that the solubility of a salt is decreased by the presence of compounds having a common ion with it; thus the solubility of silver acetate is equally affected by the presence of silver nitrate and sodic acetate.

10. The theory of "isohydric" solutions leads up to the important point of the neutralisation of acids by bases. In the first place, salts in dilute solutions are no longer considered to be the product of a reaction like the following:



Where there is perfect dissociation, at extreme dilutions, the reaction is represented thus:



At greater concentrations this is accompanied by a certain reassociation of $K + Cl$ and a dissociation K , OH and H , Cl , but $K + Cl$ is supposed to be very small in all cases, as the dissociation of salts proves to be relatively very great. Neutralisation would therefore practically mean a formation of water from H and OH , and salts as such would only exist in concentrated solutions or as a combination of a very weak acid with a very weak base. A result of this would be that the heat of neutralisation in dilute solutions should be the same for all sorts of strong acids and bases, and should, in fact, equal that produced by the reaction $H + OH$, a very familiar fact. Mixtures of such salts should not be accompanied by a heat effect, which explains the phenomenon of thermo-neutrality. But a weak base or a weak acid introduces the positive or negative heat of dissociation pertaining to it; consequently the thermal effect of neutralisation must vary from that of $H + OH$, but this variation must decrease with the increase of temperature. If a stronger and a weaker acid are together mixed with a base, it is only the *weaker* anion which really *unites* with the metal, to a limited extent, while the stronger anion keeps the relatively greater amount of metal in electrolytic dissociation, *their* neutralisation being characterised by the union of their former conjugates $H + OH$. It is noticeable that electrolytic dissociation is to be sharply separated from the *hydrolysis* of sugars and of very weak salts like ammoniac acetate, in which the reaction belongs rather to the class of non-electrolytes, although electrolytes are involved.

A final point with regard to chemical equilibrium is this, that when equilibrium has been reached in a solution containing a number of electrolytes, each one of these is in a state of dissociation, which depends upon the equilibrium of osmotic pressure between the non-dissociated molecules and all the free ions of the kinds which compose it. A distribution of metals and acids as it is usually assumed in older views is therefore rendered out of question, because a *free* ion belongs neither to one compound nor to another, it merely counterbalances that free ion of opposite charge nearest which it happens for the moment to be.

Having sketched Arrhenius' hypothesis, with some of its logical consequences, the task of judging it must be left to those readers who will compare the mass of experimental material and will convince themselves of the simple relations which the various phenomena appear to bear toward each other. As far as this test is concerned, the hypothesis will be found to fulfill its purpose. Shall it therefore be accepted?

The objections which have been raised are twofold, physical

and chemical. Prof. O. J. Lodge concedes the ingenuity and physical "orthodoxy" of the treatment, and it might appear that his criticisms to the earlier papers have been largely obviated by the further development of the theory; indeed they apply chiefly to points which I have omitted as no longer seeming essential to the theory, such as relations between the viscosity and the friction which a solvent opposes to the motion of the ions. But he appears mainly to object to the neglect of conduction by the solvent, which he believes would explain the rate of transference of the ions, without the assumption of unequal velocities of negative and positive ions. It is doubtful whether such an explanation would also elucidate the troublesome diffusion phenomena as well as does "dissociation" in the hands of Nernst. E. Wiedemann thinks that hydrates are the cause of better conduction, and explains osmotic anomalies by the assumption of a polymerisation of the solvent. Aside from Planck's proof, on thermodynamic grounds, that such polymerisation would not affect the vapor tension phenomenon in this way, in very dilute solutions, Ostwald pertinently asks why the electrolyte need cause a polymerisation which no non-electrolyte does.

The objections from a chemical standpoint have been chiefly raised by Prof. H. E. Armstrong, and are not all cogent. The following appear to be the most important at the present time:

1. Anhydrous hydrochloric acid and pure water do not conduct, while fused silver iodide does, which is an anomaly. Arrhenius finds an explanation in the dissociation of silver iodide by heat.

2. Hydrochloric, hydrobromic and hydriodic acids differ markedly in stability, but they are all assigned the same dissociation ratio. This is evidently a case of misapprehension, as the instability lies in the negative ion itself, and not in the compound.

3. Why does not alcohol dissociate electrolytes as well as water, and why does not water conduct?

4. According to Ostwald's measurements, phenylpropionic, cinnamic, and phenylpropionic acids range in the order of their conducting power,



Therefore that acid is *most* dissociated which can *least* spare its hydrogen.

This argument illustrates the necessity of keeping the types of reactions apart. Nothing appears to justify his assumption that the carboxyl group should be affected in this way by what happens in a neighboring group, where hydrogen plays an entirely different rôle.

The main opposition to the dissociation hypothesis is to be found in a rival hypothesis which has found advocates in Mendelejew, Armstrong, Pickering, Crompton, Bonty and E. Wiedemann, the "hydration" hypothesis connected with the "residual

affinity" idea. Bonty holds that electrolytes are of two classes, those in which both ions show equal rates of transference, and the "abnormal" ones, in which this is not the case. All abnormal salts are said to be capable of forming hydrates and to do so. The law of equivalent ratio holds in so few cases, absolutely, that these considerations may be dismissed, in view of the more powerful ideas of Kohlrausch. E. Wiedemann argues from the change of color of salts of nickel, copper, cobalt, etc., upon dilution and heating, effects which Arrhenius ascribes to a difference in color between the free ion and the compound. Armstrong and Pickering present the "residual affinity" theory with much vigor. The atomic valences are not assumed to be whole numbers, so that it rarely happens that the positive and negative valences in a compound just balance. Consequently, a small residual affinity remains to each molecule, by virtue of which larger aggregations are formed, molecular compounds, either among the molecules of the same sort or with the molecules of the solvent. Armstrong's valences represent the old Berzelian negative and positive electricities, which cause their respective atoms to tend to opposite electrodes during the passage of the current, the atoms being set free by the complexes "straining" at each other as they pass each other. The idea of unequal electrical charges appears incompatible with Faraday's law that the current produces the same effect in all electrolytes. Pickering bases upon more modern ideas, separating affinity from electric charges, and sees in the phenomena of electrolysis and dilution effects of the dissociation and formation of various hydrates. The basis for this lies in the observation by Mendelejew, Pickering and Crompton, that various properties of acids and salts, such as conductivity, density, the heat of solution, when plotted as ordinates, with the percentage composition of the solution as abscissas, do not present regular curves. A study of their first or second differentials would appear to reveal the presence of points of abrupt change, and these points are supposed to represent definite chemical compounds. It does not appear that Arrhenius has entirely invalidated the proofs of the existence of such compounds, and there is no doubt that they present a very awkward obstacle to his theory which he has still to surmount. On the other hand, Pickering's explanations of the phenomena of freezing are extremely complex, and I am not aware of any positive attempt to explain facts like diffusion upon them. The thermo-chemical phenomena might be fairly explained by Pickering's reasoning.

9 MORRIS LOBB.

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GRUNDRISS DER ALLGEMEINEN CHEMIE. Von W. Ostwald. Leipzig, 1889, Engelmann. pp. 402.

A sincere admirer of Professor Ostwald's monumental *Lehrbuch* must regret that the present text-book should have been chosen to present the recent developments of physical chemistry, rather than a second edition of the earlier, larger work. While the present volume is intended, according to the preface, to interest in physical chemistry those as yet unacquainted with the subject, it seems questionable whether this object can best be obtained by cutting away much that renders the larger work such delightful reading; nor does it seem plausible that a non-mathematical mind should grasp a mathematical formula better because the strict proof is omitted as too abstruse, and that the reader who is conversant with calculus should therefore be debarred from this aid to the comprehension. There is no doubt, however, that this little volume gives all the subject-matter proper of the two older volumes, with some additions; condensation has been obtained by employing smaller type, omitting many tables and much purely historical matter, and, finally, by omitting all references to titles of papers, instead of which the year of publication has been inserted in the text. The chapters have been rearranged into a very logical sequence, and the new points of view introduced by the hypothesis of osmotic pressure receive a very full and withal very comprehensible treatment.

For such as desire a rather hurried glance over a large field, this book can be very well recommended; but it is to be hoped that its presence in the chemist's library will not be supposed to atone for the absence of the *Lehrbuch*.

M. L.

AMERICAN CHEMICAL JOURNAL.

Contributions from the Laboratory of Cornell University.

THE ACTION OF DILUTE NITRIC ACID ON ACETONE.

BY SPENCER B. NEWBURY AND W. R. ORNDORFF.

The action of strong nitric acid upon ketones has been studied by Chancel and others, and has been found to result in the decomposition of the ketones at the point of the carbonyl group, with the formation of fatty acids and nitro-compounds. Other powerful oxidising agents, as chromic acid and permanganates, have been shown by Wagner and Hercz to decompose acetone into carbon dioxide and acetic and formic acids. No experiments on the gradual oxidation of acetone by dilute nitric acid are recorded, and it seemed to the authors that an investigation of this action would be of interest. It is well known that Debus,¹ by the action of dilute nitric acid on alcohol, obtained glycolic and glyoxylic acids. Similarly Lubjawn² obtained glyoxal from aldehyde; the oxidation in both cases taking place in the methyl group. It was thought probable by the authors that similar treatment of acetone might yield products of oxidation without breaking up the molecule. This expectation was proved, however, to be unfounded, and the experiments led to results very different from those which were anticipated.

Commercial acetone, purchased from Roessler & Hasslacher, was thoroughly dried by boiling for several hours with calcium chloride, and carefully distilled through a long Hempel tube. All but a slight residue passed over between 56.4° and 56.6°.

¹ Ann. Chem. (Liebig) **100**, 1.

² Ber. d. chem. Ges. **14**, 1713 and 2685.

1000 grams of strong nitric acid (sp. gr. 1.42) was mixed with 1200 grams of water, and the mixture allowed to become quite cold. 1000 grams of purified acetone was then added. No rise of temperature took place on the addition of the acetone. The mixture was placed in tall glass cylinders, and a few drops of fuming nitric acid introduced at the bottom of each by means of a long pipette. In a few hours bubbles of gas began to rise in the liquid; this gas was found to contain considerable quantities of carbon dioxide. The gradual evolution of gas continued steadily for several weeks. At the end of two months the reaction had nearly ceased. The liquid, which then smelled strongly of hydrocyanic acid and acetic acid, was poured into a large evaporating dish and allowed to evaporate spontaneously during the whole summer. After several months large crystals were found in the syrupy residue. These crystals were recrystallised from water, and on examination proved to consist of ammonium tetroxalate and free oxalic acid. On further evaporation of the syrupy mother-liquor and cooling the liquid by means of ice, a large quantity of crystals, the chief product of the reaction, separated out. These were extremely soluble in water, had a strong acid reaction, and showed the characteristic properties of oxy-isobutyric acid. In order to prepare the zinc salt for analysis a portion of the original syrup was boiled with zinc oxide until nearly neutralised, filtered, and the insoluble residue exhausted with boiling water. On cooling, zinc oxy-isobutyrate crystallised out, and after recrystallisation was analysed with the following results:

	Found.		Calculated for
	I.	II.	$\text{Zn}(\text{C}_4\text{H}_7\text{O}_3)_2 + 2\text{H}_2\text{O}.$
Loss of water at 110° ,	11.74	11.72	11.72
Zinc,	21.37	21.32	21.17

The silver salt was prepared, and yielded the following results:

	Found.		Calculated for $\text{AgC}_4\text{H}_7\text{O}_3.$
	I.	II.	
Ag	51.14	51.14	51.18

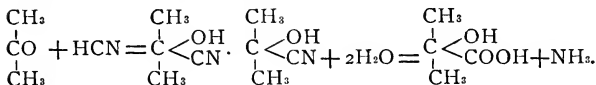
The mother-liquor from the zinc oxy-isobutyrate, containing the zinc salts of any other acids present together with any neutral products of the reaction, was found to yield only a few drops of oily liquid on exhaustion with ether. On precipitating the zinc from the solution by hydrogen sulphide, filtering, and evaporating the filtrate, vapors of nitric acid escaped and some ammonium nitrate crystallised out. The mother-liquor was precipitated with

lead acetate, the lead salts suspended in water and decomposed with hydrogen sulphide. On evaporation to dryness a very small quantity of a crystalline acid substance was obtained, the quantity of which was, however, too small to admit of its identification.

These experiments show that in the action of dilute nitric acid on acetone, carbon dioxide, acetic acid, oxalic acid, hydrocyanic acid, and ammonium salts are produced, together with a large quantity of oxy-isobutyric acid. Neither pyruvic acid nor other products of simple oxidation without a breaking up of the acetone molecule are formed in perceptible amounts.

The liberation of hydrocyanic acid on oxidation of various organic compounds by nitric acid has often been observed. According to Hantzsch,¹ this is probably due to the reduction of nitric acid to nitrous acid, and the consequent formation of iso-nitroso compounds. These, on further oxidation, break up with the formation of iso-nitroso-methane, CH_2NOH , which spontaneously decomposes into water and hydrocyanic acid.

The formation of oxy-isobutyric acid by the action of hydrocyanic acid and hydrochloric acid on acetone was observed by Staedeler,² and is a well-known method of preparation of this substance. The nitrile of oxy-isobutyric acid is first formed, and then decomposed in presence of water and hydrochloric acid into ammonia and oxy-isobutyric acid.



These reactions doubtless correctly express the formation of this product in the action of dilute nitric acid on acetone.

LABORATORY OF CORNELL UNIVERSITY, Aug. 1, 1890.

THE ACTION OF PROPIONIC ALDEHYDE ON ALCOHOLS.

BY SPENCER B. NEWBURY AND M. W. BARNUM.

The synthesis of acetal by heating aldehyde and alcohol together with a small quantity of glacial acetic acid, was accomplished by Geuther³ in 1863. Subsequently Alsberg and others applied the

¹ Ann. Chem. (Liebig) 222, 65.

² Ibid. 111, 320.

³ Ibid. 126, 63; Jahresber. 1864, 495.

same reaction to other aldehydes and alcohols, and obtained a series of products similar in constitution to acetal. Among these experiments the action of propionic aldehyde on alcohols appears not to have been studied. It was therefore thought to be of interest to ascertain whether this substance will enter into combination with alcohols in the same manner as ordinary aldehydes.

1 volume propionic aldehyde, 2 volumes ethyl alcohol, and $\frac{1}{2}$ volume glacial acetic acid were heated in closed flasks to 100° for twelve hours. The product was shaken repeatedly with a strong solution of calcium chloride to remove unchanged alcohol, dried, and submitted to fractional distillation. A large yield was obtained of a colorless product, possessing nearly the odor of ordinary acetal, and boiling at 122.8° under a barometric pressure of 74.4 cm. Analysis gave the following results:

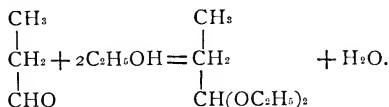
	Found.		Calculated for $C_7H_{16}O_2$.
C	63.87	63.86	63.63
H	12.32	12.08	12.12
O	24.25

The vapor density, determined by Hofmann's method, was found to be as follows:

Found.	Calculated for $C_7H_{16}O_2$.
4.564	4.574

The specific gravity of the liquid at 0° was found to be 0.8825.

These results show the product to be propionic acetal, or *propylidene di-ethyl ether*, the next higher homologue of acetal, formed by the reaction,



By heating together propionic aldehyde, methyl alcohol and glacial acetic acid, *propylidene di-methyl ether* was obtained. It was found to boil at 86° – 88° , and on analysis gave the following results:

	Found.	Calculated for $C_6H_{12}O_2$.
C	58.01	57.69
H	11.49	11.53
O	...	30.78

The specific gravity of the liquid at 0° is 0.8657.

THE ADDITION OF THE ELEMENTS OF ALCOHOL
TO UNSATURATED COMPOUNDS.

I.—THE ACTION OF ALCOHOL ON ACROLEIN.

BY SPENCER B. NEWBURY AND E. M. CHAMOT.

According to Alsberg,¹ acrolein when heated with alcohol and glacial acetic acid yields *iso-tri-ethylin*, $\text{CH}_3 - \text{CH}(\text{OC}_2\text{H}_5) - \text{CH}(\text{OC}_2\text{H}_5)_2$. Tawildaroff,² however, on repeating Alsberg's experiments, failed to obtain this product. The question whether an unsaturated aldehyde behaves like a saturated one, combining with two molecules of alcohol to form an acetal, or whether a further addition of alcohol takes place at the point of unsaturation, appeared of so great interest that the authors were led to study this reaction with care.

Acrolein was prepared according to the instructions of Fischer (*Organische Präparate*, p. 30). This method was found to give a very satisfactory yield if thoroughly dehydrated glycerine and anhydrous potassium bisulphate were employed.

As described by Alsberg, 1 volume acrolein, 3 volumes alcohol, and $\frac{1}{2}$ volume glacial acetic acid were heated for eight hours at 100° in a closed flask. On distilling the product on a water-bath, alcohol and ethyl acetate passed over, and a large amount of tarry matter remained in the flask. It was found by experiment that acrolein is completely decomposed, forming tarry products, when heated to 100° with glacial acetic acid. It is therefore evident that the reaction described by Alsberg does not take place under these conditions.

In order to avoid, if possible, the use of acetic acid, the experiment of heating ordinary aldehyde with alcohol alone was tried. To the surprise of the authors, this method was found to yield far more acetal than when glacial acetic acid was employed. 30 cc. aldehyde and 60 cc. alcohol, heated eight hours at 100° gave 38 cc. acetal (boiling from 100° to 105°), as compared with only 8 cc. when the same quantities were heated with the addition of 15 cc. glacial acetic acid.

1 volume acrolein and 3 volumes absolute alcohol were heated for 15 hours at 100° in a closed pressure-bottle. On distillation on the water-bath, nearly the whole of the product passed over, and proved to consist of unchanged alcohol and acrolein.

¹ Jahresber. 1864, 495.² Ber. d. chem. Ges. 12, 1487.

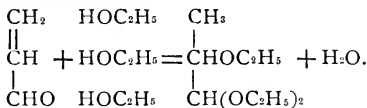
Heating for a longer period at lower temperature gave, however, more satisfactory results. The mixture of acrolein and alcohol in the above proportions was kept at a temperature of 50° for five days. On shaking with a strong solution of calcium chloride nearly the whole of the product separated as an oily layer. This was dried and distilled *in vacuo*, since it proved to decompose somewhat on distillation at ordinary pressure. The purified product is a light colorless liquid, possessing a fruit-like odor, boiling at 85° under a pressure of 1.1 cm. of mercury, and at 180°–185°, with considerable decomposition, at ordinary pressure. Its specific gravity at 0° is 0.8959. It does not decolorise bromine-water, and is therefore not an unsaturated compound. Analysis of the product gave the following results:

	Found.		Calculated for $C_9H_{20}O_3$.
C	61.18	61.04	61.36
H	11.20	11.25	11.39
O	26.25

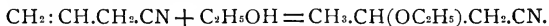
Determination of the specific gravity of the vapor by Hofmann's method in vapor of amyl alcohol gave the following result:

Found.	Calculated for $C_9H_{20}O_3$.
6.10	6.096

These results indicate that the product of the action of acrolein on alcohol is *iso-triethylin*, or *tri-ethoxy-propane*, as stated by Alsberg. The boiling point, properties, and method of preparation of this compound are, however, different from those stated by the above author. It appears, therefore, that acrolein combines with three molecules of alcohol, in the following manner:



This combination of alcohol with unsaturated compounds has been observed in other cases, notably in the formation of the nitrile of ethoxy-butyric acid by the action of alcohol on allyl cyanide, studied by Rinne¹ and Pinner.²



The position of the third ethoxy-group in tri-ethoxy-propane is not established. The difference between the boiling point of this

¹ Ber. d. chem. Ges. 6, 389.

² Ibid. 12, 2056.

substance and that of propionic acetal (described in the foregoing paper) is, however, nearly the same as that between the boiling points of acetal and ethoxy-acetal. This fact and the ready decomposition of the substance on boiling may be taken as an indication that the third group occupies the α -position, and that the compound possesses the formula $\text{CH}_3\text{CH}(\text{OC}_2\text{H}_5)\text{CH}(\text{OC}_2\text{H}_5)_2$ assigned to it by Alsberg.

On heating with anhydrous oxalic acid, acrolein is formed, together with higher products showing the boiling point of ethyl oxalate.

II.—THE ACTION OF CROTONIC ALDEHYDE ON ALCOHOL.

BY SPENCER B. NEWBURY AND W. S. CALKIN.

The peculiar behavior of acrolein with alcohol, observed by Alsberg, and described in the foregoing paper, led the authors to take up the study of the action of the next higher homologue of acrolein, crotonic aldehyde, upon alcohol under similar conditions. The object of the investigation was to determine whether a simple acetal would result by combination with two molecules of alcohol, as in the case of saturated aldehydes, or whether a further addition of alcohol would take place at the point of unsaturation, as in the case of acrolein.

Preparation of crotonic aldehyde.—The preparation of crotonic aldehyde by the usual methods (action of hydrochloric acid or zinc chloride on aldehyde) is a tedious and uncertain operation. The method suggested by Arthur Michael¹ for the preparation of aldol by the action of potassium carbonate on aldehyde, has, with certain modifications, led the authors to a most excellent process for the preparation of crotonic aldehyde. It was found that the dry potassium carbonate employed by Michael might with advantage be replaced by a dilute solution of the same substance, resulting in a great saving of time and increased yield of product. The method finally adopted is as follows:

10 grams of dry potassium carbonate is dissolved in 200 cc. of water and the solution cooled by standing in ice-water; 200 grams of aldehyde (prepared by distilling paraldehyde with a small amount of dilute sulphuric acid with the aid of a long Hempel tube), also cooled to zero, is gradually added to the

¹ This Journal 5, 190.

solution of potassium carbonate. The aldehyde dissolves completely without apparent action if the solution is kept thoroughly cooled. After adding the aldehyde the bottle containing the mixture is allowed to stand four or five hours at the temperature of the room. At the end of this time the solution will be found to be slightly yellow and of a syrupy consistence. This is then exhausted three times with ether, and the ethereal extracts united and distilled on a water-bath. A syrupy residue is thus obtained, nearly equal in weight to the amount of aldehyde employed, and consisting almost wholly of aldol. The aldol may be purified by distillation *in vacuo*, but for the preparation of crotonic aldehyde it is simply necessary to distill the syrup from a flask with the aid of a long Hempel tube. Crotonic aldehyde and water pass over, with small quantities of ether and aldehyde. The crotonic aldehyde is separated from the water by addition of calcium chloride, dried, and rectified. In this manner a quantity of crotonic aldehyde equal to thirty per cent. of the aldehyde employed may be obtained in a single day.

Action of crotonic aldehyde on alcohol.—Mixtures of crotonic aldehyde and alcohol, in the proportion of one molecule of the former to three of the latter, were heated together at varying temperatures up to 100° for periods ranging from a few hours to several days. In all cases the two substances were found quite unchanged, no combination between them having taken place. No result was obtained on heating the mixture with a small amount of glacial acetic acid. The addition of zinc chloride, however, caused the combination to take place readily.

60 grams crotonic aldehyde was added to 120 grams absolute alcohol, and 30 grams dry zinc chloride dissolved in the mixture. The solution was then heated in closed bottles for six days at a temperature of 50° . At the end of this time the solution had become reddish in color, and the odor of croton aldehyde had almost wholly disappeared. The mixture was shaken with strong calcium chloride solution to remove unchanged alcohol, dried, and submitted to fractional distillation. A small quantity of a higher product was present, which decomposed on distillation and rendered the purification of the chief product difficult. This was finally obtained as a colorless liquid of pleasant fruit-like odor, boiling with slight decomposition at about 190° . Under a pressure of 15 centimeters of mercury it boils without decomposition at 88° to 90° .

On analysis the following results were obtained :

	Found.		Calculated for $C_{10}H_{22}O_3$.
C	62.84	62.96	63.16
H	11.58	11.43	11.58
O	25.26

Determination of the specific gravity of the vapor of the substance by Hofmann's method in vapor of amyl alcohol (b. p. 130°) gave the following result :

	Found.	Calculated for $C_{10}H_{22}O_3$.
	6.588	6.669
		6.581

The specific gravity of the liquid at 0° was found to be 0.8825.

These results indicate that the substance is *tri-ethoxy-butane*, probably possessing the formula



homologous with the corresponding compound obtained in a similar manner from acrolein. The position of the third ethoxy-group is of course uncertain. The comparatively slight difference between the boiling points of this compound and of the tri-ethoxy-propane described in the foregoing paper, together with the decomposition of both substances on boiling, may serve as a slight indication that the two compounds possess a similar constitution, and that the tri-ethoxy-butane obtained by the authors possesses the formula $CH_3.CH_2.CH(OC_2H_5).CH(OC_2H_5)_2$. It is hoped that experiments now in progress on the action of alcohol on unsaturated acids may throw further light on the position taken by the third ethoxy-group in the above reaction.

These experiments show that crotonic aldehyde enters into combination with three molecules of alcohol in the same manner as acrolein, the combination taking place, however, far less readily than in the case of the latter substance.

Contributions from the Chemical Laboratory of Wesleyan University.

IV.—THE ACQUISITION OF ATMOSPHERIC NITROGEN BY PLANTS.¹

BY W. O. ATWATER AND C. D. WOODS.

REPORTED BY W. O. ATWATER.

Until within a few years it has been the prevalent, though not universal, opinion of chemists and vegetable physiologists that the free nitrogen of the air is not assimilated by plants, and that, as the proportions of combined nitrogen in the atmosphere are so minute that the amounts which ordinary plants could absorb during their growth must be unimportant, nearly all of the nitrogen of plants is furnished to them by the soil, either from previously accumulated stores or from fertilising materials applied to it. In 1881 the writer instituted a series of experiments, which were repeated in 1882, and brought positive evidence of the acquisition of large quantities of nitrogen from the air by peas during their period of growth. The investigation was unavoidably interrupted until 1885, when four other series revealed large losses of nitrogen during germination and early growth. In the account of these later investigations it was urged that this loss of nitrogen was probably caused by microbes; that it helped to explain why previous experimenters had failed to find proof of the acquisition of atmospheric nitrogen by plants, especially legumes, but that the negative results obtained by the latter were also due to the exclusion of the action of electricity or microbes, by which the assimilation of atmospheric nitrogen might be aided.²

The circumstances which caused the cessation of the investigation from 1883 to 1885 were alike operative from the latter time until 1888. Meanwhile the very important investigations of Hellriegel³ and others had confirmed those of the first and second

¹ Reprinted, with some alterations, from the Report of the Storrs (Conn.) Agricultural Experiment Station for 1889. A brief account of the experimental results was published in Bulletin No. 5 of that Station, October 1889.

² The results of the experiments of the first series were reported briefly at the meeting of the American Association for the Advancement of Science in 1881, those of the first and second series together were reported at the meetings of the British and the American Association for the Advancement of Science in 1884, and in detail in this Journal 6, 365 (February, 1885). Those of series three to six were reported in this Journal 8, 327 and 398.

³ Hellriegel and Wilfarth, *Unters. u. d. Stickstoffnahrung der Gramineen und Leguminosen*, Beilageheft z. d. Zeitsch. des Vereins f. d. Rübenzucker-Industrie d. D. R., Nov. 1888.

series referred to, and while bringing additional evidence of the acquisition of atmospheric nitrogen, had also indicated the very strong probability that micro-organisms are active agents in the assimilation of nitrogen.

The experiments herein described are a continuation of the previous ones in this place. The methods are also similar, save that the introduction of soil infusions and observations on root tubercles were suggested by the experience of Hellriegel.

The specific question for study in the first series of experiments here was:

(1) May plants (peas), grown under normal conditions acquire any considerable amount of nitrogen, free or combined, from the air?

The second series was planned to verify the strongly affirmative results of the first and to include the collateral inquiry:

(2) How is the acquisition of nitrogen from the air affected by abnormal conditions of growth?

In the present investigation the study of the first question is continued with peas and other plants, legumes and cereals, and the two further questions have been included:

(3) What effect has the addition of soil infusions upon the formation of root tubercles under the conditions of the experiments?

(4) Is there a definite relation between the quantity or number of root tubercles and the quantity of atmospheric nitrogen obtained by the plant?

Previous Experiments in Middletown.

Before entering upon the details of the work to be reported herewith, a recapitulation of the experiments of the first two series above referred to may be appropriate. The plan of the experiments was similar to that of the ones to be reported beyond. The plants were grown in purified sand, supplied with solutions of appropriate salts including nitrogen and nitrates, and kept in open air, but protected from rain and dew. The first series included five, and the second, twelve experiments. The figures of numbers five to twelve of the second series given in the table herewith will, with the explanation quoted, suffice to illustrate the results obtained.

The "concentrated" solutions contained from 2.5 to 6, and the

"dilute" from 0.3 to 1.6 parts of water-free salts in 1000. A concentration of 1 per 1000 has elsewhere been found favorable, and one of over 2 per 1000 unfavorable to normal assimilation.¹

The well-fed plants had quantities of mineral food estimated to be sufficient for their nourishment, the scantily-fed ones, one-half as much. The "larger nitrogen ration" was estimated to supply an amount of nitrogen rather small in proportion to the mineral food, and the "smaller nitrogen ration" less than one-half as much as the larger. The gain or loss of nitrogen is computed by adding to the amount of nitrogen in the plants the amount left in the nutritive solution at the end of the experiment, and subtracting from their sum the sum of the amounts in the seed and in the nutritive solution at the start. The figures for "apparent gain or loss" represent, therefore, the quantities acquired from the air less whatever may have been liberated from solution or seed or plants during growth.

Statistics of Experiments on the Assimilation of Atmospheric Nitrogen by Peas.

Conditions of Experiments.			No. of Experiments.	Nitrogen Supplied.			Nitrogen found at End of Experiment.			Apparent Gain + or Loss — of Nit'g'n.
				In Seeds.	In Nutritive Sol'n.	Total.	In Plants.	In Residual Sol'n.	Total	
				Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.
Larger Nitrogen Ration,	Concentrated Solution,	Scantily fed,	3	70.3	136.9	207.2	197.5	12.7	210.2	+ 3.0
		Well fed,	6	34.8	136.9	171.7	149.6	1.2	150.8	— 20.9
	Dilute Solution,	Scantily fed,	12	68.8	136.9	205.7	260.2	45.7	305.9	+ 100.2
		Well fed,	10	34.6	136.9	171.5	277.8	35.7	313.5	+ 142.0
Smaller Nitrogen Ration,	Concentrated Solution,	Scantily fed,	7	71.5	59.4	130.9	158.1	0.0	158.1	+ 27.2
		Well fed,	5	34.2	59.4	93.6	156.1	0.0	156.1	+ 62.5
	Dilute Solution.	Scantily fed,	11	72.5	59.4	131.9	210.9	2.7	213.6	+ 81.7
		Well fed,	9	35.3	59.4	94.7	186.5	1.4	187.9	+ 93.2

The following statements are from the summary of the conclusions, which embodies also those of the four series of experiments on the liberation of nitrogen during germination and the early growth of peas above referred to as undertaken in connection with this investigation :

1. "The experiments showed in some cases a large acquisition of nitrogen from the air, the gain amounting in some instances to half or more than half of the whole nitrogen in the plants.

¹ We have found plants to grow well in more concentrated solutions (see also Hellriegel, Naturwiss. Grundlagen des Ackerbaus), but in these experiments, at any rate, there was less apparent gain of nitrogen with the concentrated than with the dilute solutions.

In other cases there was, apparently, a very small gain or a loss of nitrogen. There seems to be excellent ground for assuming that the cases in which either only a small gain or a loss of nitrogen was observed (in all of which the conditions of growth were abnormal) are to be explained by the escape of nitrogen either from the nitrates of the nutritive solution or from the seeds during germination, or from the growing plants. The proof of the acquisition of atmospheric nitrogen which is furnished by the cases in which the conditions of growth were normal, in each of which the amount acquired was large, is thus rendered the more emphatic. The faculty of obtaining nitrogen from the air appears to be especially characteristic of the legumes. By what species of legumes or other families of plants it is possessed, it is as yet impossible to say.

2. "The liberation of nitrogen appears to be due, in some cases if not in all, to ferments. To explain why it should take place in one case and not in another, is as difficult as to account for the fact that zymotic diseases attack one animal and not another, or that the plants of certain fields are affected by fungi, while others escape. It is, however, noticeable, that in nearly all the experiments in which no gain of nitrogen has been observed, the plants have been ill fed, or the nutritive solutions have been very concentrated, or other conditions have been abnormal; while, so far as the details at hand show, the largest gains have been found in the cases where the conditions of growth were most favorable.

3. "How the nitrogen was obtained in the experiments in which its acquisition is proven, is still a matter of doubt. It must have been taken either as free or as combined nitrogen, and either directly through the foliage or indirectly through the soil and nutritive solutions and the roots of the plants.

4. "It would be going too far positively to assume that in the experiments which have given the strongest evidence against the fixation of free nitrogen by plants—namely, those of Boussingault and of Lawes, Gilbert and Pugh, in which the plants were raised under glass, in confined air, or in air washed free from nitrogen compounds—the negative results are due to the escape of nitrogen in the manner above suggested, though such liberation cannot be regarded as impossible. But it is at least conceivable that the measures adopted to exclude nitrogen compounds—keeping the plants under glass and passing the air through acid and alkali

solutions before entering—may have excluded the action of electricity or of microbes, by which the fixation of free nitrogen may perhaps be effected. The plants were also, for the most part, very poorly fed. That this may be the cause of deficient assimilation of nitrogen is indicated by the experiments with peas above referred to. At any rate, until we know more about the relations of electricity and of micro-organisms to the fixation of nitrogen, we can hardly be warranted in assuming that these experiments prove that plants grown under normal conditions do not assimilate the free nitrogen of the air.

5. "To what extent the attested acquisition of atmospheric nitrogen is a function of the plant alone; in how far it may be dependent upon the action of electricity, microbes, or other agency induced by the plant; by what species of plants and under what conditions it is accomplished, are of course matters for further study. The experiments of Berthelot imply that organic matter, through the agency of electricity, and soils containing clay, through the agency of living organisms, may fix the free nitrogen of the air. It may, hence, be inferred that in some of the experiments in which acquisition has been observed, the nitrogen may have been first taken from the air by the medium in which the roots grew and communicated through the latter to the plants. But in my experiments this medium consisted of ignited sea sand and an aqueous solution of salts. I am aware of no observed facts to imply that these, separately or together, are able to fix free nitrogen by aid of electricity, micro-organisms, or any other means. In the present state of our knowledge, therefore, the balance of probability seems to decidedly favor the assumption that the plants themselves must be factors in the acquisition of atmospheric nitrogen.

6. "Messrs. Lawes, Gilbert, and Warrington have shown the great probability that the legumes, which appear to possess in high degree the power of obtaining nitrogen from natural sources, induce the action of nitrifying ferments by which the inert nitrogen of the soil is made available. It is equally conceivable that the same plants and others may favor the action of nitrogen-fixing micro-organisms."¹

¹ See, however, later views and experiments by Messrs. Lawes and Gilbert, *Phil. Trans.* 1889, 1, and especially *Proc. Roy. Soc.* 47 (1890), 85.

Plan of the Experiments here Reported.

The plants in the experiments here described were all grown in purified sea sand. A number of trials were made by water culture, and two (with corn) in ordinary garden soil. A difficulty with the last is that no method which we have as yet been able to find for the determination of nitrogen will admit of its estimation with the desired accuracy in the large amount of soil needed for satisfactory development of the roots.

Effort has been made to grow the plants under conditions as nearly normal as is consistent with a rigid control over the supply of nitrogen. To this end an abundance of plant food (nitrogen excepted) in not too concentrated solutions, room for the development of roots, exposure to sun and air, and protection from wind, rain, dew and excessive heat, have been provided.

An exact account of all nitrogen supplied the plants, aside from that brought to them by the air, was kept, and at the end of the experiment the nitrogen in the whole plant, as well as that left unused in the nutritive solution, was determined. The difference between these two amounts must show the loss or gain in nitrogen. A loss must indicate decomposition either of the organic nitrogen of the seed or plants or of the nitric acid of the nitrates fed, or of both. A gain must represent nitrogen acquired from the air in excess of any lost either from the organic matter of the seed or plant, or from the nitrates of the food.

Appliances, Materials, and Methods.

Shelter.—In lack of a satisfactory greenhouse, a temporary structure was built with board walls and "three-quarters" roof. The board walls were five feet high at the front and side and higher at the back. At the front and sides the boards were hinged so as to open conveniently. The end gable walls were of canvas, buttoned like an ordinary carriage curtain. The canvas roof opened and closed with a roller, somewhat like an ordinary roll awning. The roof is steep and has usually proved an ample protection from the rain, though in a long-continued storm the past autumn the rain beat into part of the house so as seriously to interfere with one series of experiments. The canvas had become somewhat worn from use; it is doubtful if the accident would have occurred with new canvas. The house is easy to manage;

two minutes are sufficient in which to close and thoroughly secure it at night or before a storm, and still less time is needed to open it.

By this arrangement the plants are grown in the open air in pleasant weather and protected from rain and dew by being kept under cover at night and in rainy weather. In the few cases when the sun's heat was excessive the roof was closed, leaving the sides open. The white canvas allows considerable light to penetrate and more or less air to circulate at all times, and the plants have not suffered materially even when, as occurred more than once during the past summer, it was necessary to keep the house closed for several days at a time. The extreme humidity of the atmosphere, which caused the plants to become "drawn" or young plants to "damp off," in gardeners' phrase, is the greatest drawback we have found, and this seemed to be due more to the extraordinary wetness of the past season than to the kind of house employed. Of course it is not such an arrangement as is to be desired, and more satisfactory results are expected in a greenhouse, which it is hoped may be built for the purpose.

Pots.—For pots in which to grow the plants, ordinary glass bottles with their bottoms cut off, or bell jars with open tops, varying in capacity from one to twenty liters, were employed. They were turned neck downwards, a watch-glass was placed over the neck of each and the sand poured in until they were filled within one or two centimeters of the top. Moistening the sand before putting into the jar to avoid too close packing has not been found necessary in our experiments. A glass beaker was placed under the mouth of each pot to catch any solution or sand that might run through. This simple and inexpensive arrangement has served its purpose most satisfactorily. The drainage insures against excess of water and provides circulation of air without the use of glass, pebbles, cotton, tube for conveying air to the bottom, or other arrangements that have been recommended for the purpose.¹ The pots were enclosed in wooden boxes so constructed as to afford easy access by a door in the side. In our earlier experiments each pot was placed in a box by itself²; in the later work it has been found less expensive and more convenient to put a number of pots, sometimes twelve or more, in one box.

Soil.—Sea sand was freed from coarse particles by sifting,

¹ See Hellriegel, *Naturwiss. Grundlagen des Ackerbaus*, S. 767.

² This *Journal* 6, 367.

thoroughly washed with water, and ignited at a red heat for some time. The sand thus treated gave, in repeated tests, no trace of nitrogen by either the soda-lime or the Kjeldahl method.

Food Supply.—The mineral elements needed for the growth of the plants were added in amounts to make one part or less by weight of dissolved salts in one thousand parts of the solution. Some of the plants received no combined nitrogen except that in the seed; to others nitrates were added, but in such small quantities that the minerals were relatively in excess; to others enough nitrogen was added to make the mixture of plant food correspond more nearly to the composition of the plants.

Seed.—Seeds were selected of normal appearance and as uniform in size and weight as practicable. After weighing, each seed was wrapped in filter paper, moistened and allowed to germinate. When the radicles were a centimeter in length or thereabouts, such seeds as germinated well were selected for planting.

Soil Infusions.—The soil infusions were prepared by treating 300 grams of soil taken from near the roots of vigorous plants, with 750 cc. of hydrant water for 24 to 48 hours, with occasional shaking. The liquid decanted with the least possible sediment constituted the "soil infusion." The maximum amount of nitrogen found by analysis in 25 cc. of soil infusion was 0.4 mg.; the minimum, 0.06 mg.; and the average of 21 analyses of seven kinds of soil infusion gave 0.26 mg. of nitrogen. This amount is so very small that no account is made of it in the statements of nitrogen supplied.

Water.—The water used in these experiments was prepared by distilling well-water, which contained only minute traces of free ammonia and very little so-called albuminoid nitrogen, with the addition of sodium hydroxide and potassium permanganate. The distillate was rejected until Nessler's reagent produced no appreciable coloration. This so-called "nitrogen-free" water actually contained a minute trace of ammonia, the average of several determinations giving 0.0066 milligram of nitrogen in one liter of water. In only two of the experiments with plants were more than twenty liters of water used, and as 150 liters would, by the determinations above cited, contain only one milligram of combined nitrogen, error from the use of this water is too small to be taken into account.

Nutritive Solutions.—Four different nutritive solutions were employed. All were so prepared as to contain one part by weight of salts to one hundred parts of solution, the proportions being made as accurate as practicable by the use of chemically pure salts. In those containing nitrogen, determinations of the latter were made. The solutions were:—

Phosphoric Acid Solution.—This consisted of primary potassium phosphate (KH_2PO_4) dissolved in water in the ratio of 1 gram to 100 cc. 1 cc. contained about 5.2 milligrams P_2O_5 and 3.5 milligrams K_2O .

Magnesium Solution.—Magnesium sulphate (MgSO_4) in water, 1:100. 1 cc. contained 3.8 milligrams MgO and 6.7 milligrams SO_3 .

Iron Solution.—Ferric chloride (Fe_2Cl_6) in water, 1:100. 1 cc. contained 3.4 milligrams Fe and 6.6 milligrams Cl .

Nitrogen (N III) Solution.—Calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) and potassium nitrate (KNO_3). 1 part of each salt or two of both together to 200 parts water. 1 cc. contained approximately 1.54 milligrams nitrogen and 1.7 milligrams CaO . The "N III" solution was always supplied to the plants from the same 25 cc. pipette, which actually delivered at 16°C ., 24.895 cc. The mean of several analyses gave 37.66 milligrams of nitrogen in this quantity of the nitrogen solution used in 1888, and 37.94 milligrams in that of 1889.

When the solutions were applied, enough water was added to make the solution in the sand contain less than one part of salt to one thousand parts of water.

Preparation for Analysis.—At the end of the experiment the aerial portions of the plant were harvested and the roots separated from the sand by washing with water. The separation is easily effected, and but comparatively little water is required if the harvesting is done before the plants are too much withered and the washing follows before the roots are dried. The nitrates of the "residual solution" are first removed with water. The washings are evaporated for the determination of nitrogen in the residual solution. After the nitrates are supposed to be completely washed out, another extraction is made in each case, and the water evaporated and tested for nitrates by the same quantitative method as for the regular determination. The pots serve conveniently as funnels, and, as repeated tests have shown, but a

comparatively small amount of water is needed to wash out the nitrates completely. The pots are then supported obliquely with the surface downwards and the sand washed out by a stream of water. The roots, which suffer very little loss in this process, are dried and the nitrogen is determined in them as in the tops.

Estimation of Number of Root Tubercles.—The tubercles vary from the size of a pin head to that of a small pea, or larger, and tend to grow together in masses, so that it is practically impossible to count them, and even if counted, the number would mean but little for purposes of comparison because of the variations in size. An arbitrary estimate of their amount was, however, made at the time of the separation of the roots from the sand by washing. As this, of course, preceded the weighings and analyses, the observer was free from bias in judging of the abundance of the tubercles. When the number was so small that they could be readily counted, the roots were spoken of as having "few tubercles"; more than could be readily counted were spoken of as a "fair number," or, when they were present in great abundance, the expression "a large number" was used. The estimates are relative and depend somewhat upon the amount of roots, for what would be a large number with a small root development would be a "fair number" when distributed over a large amount of roots. This arbitrary classification, which presented but little difficulty in practice, is used in the descriptions and tables beyond.

Methods of Analysis.

Details of analyses are given in the Appendix beyond. The methods used were as follows :

Nitrogen in Seeds.—A considerable quantity of the seed was ground, and samples from it analysed by either the soda-lime or the Kjeldahl method, or both. The average of these analyses was assumed to represent the percentage of nitrogen in the seeds of the same lot which were sown in the experiment.

Nitrogen in Plants.—In the earlier work the analysis of the plants was made by grinding and estimating nitrogen by the soda-lime method, in samples of the whole and multiplying in the usual way. In the experiments here described, unless the plants weighed more than twenty-five or thirty grams, they were put into one or more Kjeldahl digesting flasks and treated directly without grinding. In an ordinary digester no difficulty was found

in handling ten grams, and as much as twenty grams have been successfully used. The only trouble is from frothing, which can be prevented by slow heating. After digesting, the solution was diluted and divided into aliquot parts for distilling, each portion being distilled and titrated by itself. By thus determining the nitrogen in the entire sample, the labor was reduced, and as no sampling was necessary, the accuracy was increased. Usually the whole solution was diluted to 300 cc. and one-third taken for each determination. For convenience in calculating, the amounts of alkali used for the back titration in each portion from one experiment were added together and their sum subtracted from the cc. of alkali solution corresponding to the total number of cc. of acid used. In this way the total nitrogen was determined, but the details of each part of the analysis were not kept distinct; hence the analytical details would only show the total amount of nitrogen found in the entire plant of a given experiment. As the chief use of details in the Appendix is to show the numbers and comparisons of determinations, the details of the determinations of the nitrogen in the plants are not given there. It may be added, however, that the triplicate determinations agreed very closely, as would be expected from the fact that the method was the same as that used for the determination of nitrogen in the seeds, of which details are given.

Nitrogen in Nutritive Solutions.—The nitrogen in the nutritive solutions and in the residual solutions extracted from the sand at the end of the experiment was determined by the method of Schulze-Tiemann. Properly manipulated this method gives very accurate results, as is shown by an investigation of the method and its sources of error, the results of which will be printed in detail elsewhere.

Notes on the Culture and the Growth of the Plants.

Like other experimenters, we have found it feasible, with proper care, to grow plants in sand culture to compare favorably with the same varieties of plants grown in the field or garden. Different species of plants require somewhat different treatment, which can be learned only by experience. On the whole our plants have succeeded better in cool than in hot weather, perhaps because of the difficulty of keeping the soil (sand) cool when the weather is hot. The tendency of peas, especially young vines, to mildew in hot,

damp weather has been very troublesome. In a long-continued wet period last July over fifty young pea plants "damped off." Numerous drawbacks of this and similar kinds have been experienced. Of 267 experiments undertaken only about 100 have proven wholly successful. Still we deem sand culture decidedly practicable and useful for the plants we have worked with.

East Hartford Early Peas.—This is an early, dwarf variety prized by market gardeners in this vicinity. In ordinary culture the vines grow from two and one-half to three feet in height and in rich soil are somewhat taller. In our experiments many of the plants attained the normal size and some were unusually large. In numerous cases peculiarities of growth demand attention. Although these peculiarities were no more marked in the plants without than in those with nitrogen in the food supplied, it will be well for convenience to consider especially the plants that were not fed with nitrogen aside from that contained in the seed. Usually the growth of these plants was reasonably uniform and apparently normal until they attained a height of twelve or fifteen inches. From this stage one of three things happened, leading to the following classification :

(1) A "starvation" period, analogous to that described by Hellriegel,¹ began, in which the healthy green color of the leaves gave place to a sickly yellow, the plants blossomed and developed small and imperfect peas or none at all, and then died. The plants manifesting this demeanor had very few, or, more commonly, no root tubercles. Experiment No. 137² illustrates this. Three seeds, weighing together 0.96 gram, gave rise to two plants fifteen inches in height, and one, ten inches in height and bearing one pod containing one pea. The dry plants weighed 0.97 gram and contained 11 milligrams less nitrogen than was contained in the seed. There were no root tubercles.

Sometimes the plants recovered from this starvation stage and developed so as to be grouped with those of the other classes.

(2) The plants retained their healthy appearance, blossomed, developed a few seeds, rarely more than one or two, and then died without attaining a greater growth. Root tubercles were usually found in greater or less abundance in this class. Experiment No. 119 is a case in point. Two seeds, weighing 0.53 gram, gave rise to two plants 18 inches high, bearing three pods and 3 peas. The

¹ Hellriegel und Wilfarth, loc. cit.

² See tables at end of this article.

dry plant weighed 1.57 grams and contained 31 milligrams more nitrogen than was in the seed used. There were a large number of root tubercles.

(3) Other plants kept on growing, were apparently normal, and frequently attained a height of four or more feet before blossoming. Usually these plants bore a fair number of perfect seeds.

In the experiments with East Hartford Early peas, from two to five plants were grown in a single pot, but in no case did all of the plants of an experiment attain this large growth. Thus Experiment No. 136 had four plants, of which three might be reckoned with the second, and one with the third class. Four seeds, weighing 0.94 gram, gave rise to three plants 14 inches high bearing three pods and containing three peas, and one plant 58 inches in height bearing two pods and nine peas. The first three plants were ripe July 1st; the other kept on growing till August 15th. The four plants weighed 7.06 grams and contained 243 milligrams more nitrogen than was in the seed used. Root tubercles were abundant.

Examples of all three of these phases of growth sometimes occurred in the same pot. As a rule, the larger the plant the greater was the number of root tubercles found upon it.

The last two phases of growth were even more noticeable in the experiments in which nitrates were supplied to the plants. Occasionally the first, or starved form, appeared. Usually the plants were relatively taller and contained higher percentages of nitrogen than those not fed with nitrates. In several cases these so-called "dwarf peas" attained a height of over eight feet.

Experiment No. 148 illustrates all three phases of growth in a case in which nitrogen was supplied in nitrates. Four seeds gave rise to four plants, 16, 35, 42 and 83 inches high respectively. The last plant had 11 peas, the other three 13. In this case tubercles were abundant on the large plants.

Champion of England Peas.—As a rule these peas grew much more uniformly than the dwarf peas, though in a single pot they often varied two or more feet in height. The different phases of growth were less marked than with the dwarf peas.

Alfalfa.—We have found but little difficulty in growing alfalfa in sand; even plants not fed with nitrogen, but supplied with plenty of mineral food, have developed normally and have at no time shown any very marked starvation-stage of growth. Two

experiments will illustrate the vigor of growth, both with and without a supply of nitrogen in the food.

In Experiment No. 109, three plants, to which no nitrogen was fed other than the small fraction of a milligram contained in the seed and soil infusion, had sixteen branches averaging 15 inches in height, and weighed, air dry, 3.22 grams. They obtained from the atmosphere 137 milligrams of nitrogen.

In Experiment No. 113, one plant fed with nitrogen in the form of nitrates, had 35 branches, averaging 20 inches in height; weighed 12.9 grams and contained when mature 382 milligrams of nitrogen more than was supplied to it in seed and nutritive solution.

Oats and Corn.—Oats grew well, better than field oats average in this climate. The corn grew fairly well, but did not fruit fully. Lack of fertilisation from insufficiency of pollen seemed to be the chief trouble. Owing to its tendency to great root development, pots of three to five gallons capacity were used.

The Experiments here Reported.

The experiments here described may be divided into the following series:

Series.	Year.	Kind of Plants.	No. of Exp'ts.	No. of Plants.
VII	1888	Champion of England Peas.....	25	64
VIII	1888-89	Alfalfa.....	5	9
IX	1888	Corn.....	8	15
X	1889	East Hartford Early Peas.....	34	104
XI	1889	Champion of England Peas.....	16	70
XII	1889	Oats.....	11	66
XIII	1889	Corn.....	18	35
Total.....			117	363

Specimen Experiments.

The methods may be illustrated by a description of two typical experiments.

Experiment No. 135, with East Hartford Early Peas, Series of 1889.—The pot used in this experiment held 3 kilograms (six and a half pounds) of sand. This was placed in the pot April 10th, and the same day four well-sprouted peas, which had weighed before sprouting 0.998 gram, were planted. When planted they were fed with mineral salts, without combined nitrogen, in such

amount that the ratio of salts to water was about 1 to 1500. They were again fed with minerals on May 10th. During the period of growth, water was given them 41 times, 6.6 liters being used. No soil infusion was given.

About the middle of June two of the plants had stopped growing. These were not more than one foot in height, and when harvested were found to have no root tubercles. The other two kept growing, though not equally well, till about July 9th, when they were harvested. At this time one of the plants was two and one-half and the other a little over five feet in height. Both had root tubercles. The four plants had 9 pods and 15 peas. The weight of the partly-dried fruit and vines was 7.97 grams. The roots, freed as far as practicable from sand, weighed 1.27 grams, making the total weight of the four plants 9.24 grams. The plant altogether contained 237.1 milligrams of nitrogen. The seed, as shown by analysis of similar ones, contained 39.9 milligrams of nitrogen. The balance-sheet of the experiment is as follows:

Nitrogen fed in the seed, . . . 39.9 milligrams.

Nitrogen found in plants, . . . 237.1 milligrams.

Gain, 197.2 milligrams.

The gain of nitrogen during the growth was thus 197.2 milligrams.

In a large number of experiments the plants have had no root tubercles. In nearly every case of this sort there has been more or less loss, instead of gain, of nitrogen. The natural inference is, that in the experiment just described all the gain of nitrogen was made by the larger plants which had the root tubercles, and that they thus actually acquired from the air not only 197.2 milligrams of nitrogen which is counted as gain, but enough besides to offset more or less loss where there were no tubercles.

Experiment No. 165, with Champion of England Peas.—Six kilograms of sand were placed in the pot April 15th, and the same day six peas, weighing 2.3 grams, were planted. The plants were fed with minerals and with nitrogen in the form of calcium and potassium nitrates, when the seeds were planted, and on May 15th, June 20th, and June 22d. On May 11th and 20th, 25 cc. of an infusion of garden soil in which peas were growing, were added. During the whole period of growth the plants were watered 46 times, 13.9 liters water being used. The plants had finished their

growth and were nearly ripe on July 9th, when they were harvested. The notes taken at the harvesting were as follows :

Six Plants Grown in Sand.

HEIGHT.		NO. OF PODS AND PEAS.	
		Pods.	Peas.
3 feet	8 inches.....	1	2
4 "	9 "	3	5
5 "	10 "	4	7
4 "	0 "	2	6
5 "	9 "	3	7
5 "	6 "	2	7
Total.....		15	34

The roots had a large number of tubercles, which were pretty evenly distributed. The partly dried vines and fruit weighed 24.85 grams, the roots, freed from sand as completely as practicable, 7.87 grams, making the total weight of the six plants 32.72 grams. These contained 694.5 milligrams of nitrogen. The soil (sand) at the end of the experiment contained 23.5 milligrams of nitrogen as nitrate. The balance-sheet is as follows :

Nitrogen fed in the seed, .	105.1 mg.	
Nitrogen fed in solution, .	447.7 mg.	
	<hr/>	552.8 mg.
Nitrogen found in soil, .	23.5 mg.	
Nitrogen found in plants, .	694.5 mg.	
	<hr/>	718.0 mg.
Gain in nitrogen,		165.2 mg.

The principal statistics of the experiments are given in the tables at the end of this article.

Absorption of Combined Nitrogen from the Air.

Tests made in connection with previous experiments here failed to give indications of any considerable absorption of ammonia or nitric acid by nutritive solutions in sand exposed to the air under conditions similar to those of the experiment, and implied that no considerable quantities of combined nitrogen from the air could have been purveyed to the plants by the solutions.¹ As a further

¹ The following is from the discussion of the experiments referred to: "During the course of the experiments of the second series, a number of pots with sand and solutions like those in which the plants grew were kept alongside the latter. The solutions at the end of the experiments revealed only such minute quantities of combined nitrogen as are commonly found in natural waters exposed to the air. That these solutions, without plants, had so little of nitrogen compounds is, however, no proof that the solutions in which the plants grew might not

precaution the following tests were made in connection with the experiments here reported. Pots were filled with sand, and nutritive solutions (see descriptions of nutritive solutions above) were added as in the regular experiments, but no seeds were sown. In two cases dilute acid was used instead of the nutritive solutions. They were put into the planthouse, July 11th, and brought to the laboratory for analysis, October 20th, 1889, and were thus exposed for over three months to the same atmospheric conditions as those in which the plants were grown. They were watered often enough to keep the sand apparently as moist as that in which the plants were grown, 1100 cc. of water being used for each pot. Eight such tests were made, in four series, as follows:

A. With Dilute Sulphuric Acid.—Two pots, Nos. 65 and 66, each holding $1\frac{1}{2}$ kg. of sand, were each supplied with 10 cc. of dilute sulphuric acid containing, approximately, 30 mg. of H_2SO_4 in 1 cc. At the end of the trial the solutions were extracted and tested for ammonia and nitric acid. Each gave by distillation and titration approximately one milligram of ammonia and no trace of nitric acid by the Tiemann-Schulze method, thus indicating that a minute quantity of ammonia and no appreciable amount of nitric (or nitrous) acid had been absorbed from the air and fixed by the acid solution.

B. With Nutritive Solutions containing no Nitrates.—Two pots, Nos. 67 and 68, each holding $1\frac{1}{2}$ kg. of sand, were each supplied with 15 cc. phosphoric acid solution, 10 cc. of the magnesium solution and 1 cc. of the iron solution used in the experiments. Extracted and tested as above, at the end of the trial neither yielded any appreciable quantity of ammonia or nitric acid.

C. With Nutritive Solutions, including Nitrates.—Two pots, Nos. 69 and 70, each holding $1\frac{1}{2}$ kg. of sand, received each 15 cc. of the phosphoric acid solution, 10 cc. of magnesium solution, 1 cc. of the iron solution, and 25 cc. N.III solution (calcium and potassium nitrates), used for the experiments. At the end of the trial both were extracted and tested, as was done with the previous series. In neither was any appreciable quantity of ammonia found. Each had received 37.66 mg. of nitrogen in the "N.III" solution.

have yielded to the plants some of the ammonia which they were continually absorbing, and which, if not somehow seized upon, would escape by virtue of its tension. The fact that the solutions in which the plants grew were neutral or faintly alkaline, would, however, make the hypothesis of any considerable absorption of ammonia apparently improbable. It is worth noting, too, that the residual solutions at the end of the experiment contained only the minutest quantities of ammonia discernible by aid of Nessler's reagent."—This Journal 6, 376.

No. 69 gave 36.66 and No. 70, 36.30 mg. of nitrogen, as nitric acid or other nitrogen compound, by the Tiemann-Schulze method. There was, then, no indication of absorption of ammonia, but very small quantities of nitrates were lost.

D. With Nutritive Solutions, including Nitrates and Pea-Soil Infusion.—Two pots, Nos. 71 and 72, each holding 2 kg. of sand, received each 15 cc. of phosphoric acid solution, 10 cc. magnesium solution, 1 cc. iron solution, 25 cc. N.III solution and 25 cc. of pea-soil infusion. At the end of the trial neither gave any appreciable quantity of ammonia. Each had received 37.66 mg. of nitrogen in nitrates. In No. 70, 36.30, and 71, 36.84 mg. of nitrogen was obtained by the Tiemann-Schulze method. The results were, therefore, essentially the same as those in series C.

It appears, then, that no considerable amount of combined nitrogen was acquired either by the nutritive solutions or by an acid solution in sand under the conditions in which the plants of the experiments were grown. Of course the solutions in which the plants grew were subject to changes different from those to which the solutions in these blank trials were exposed, but it is difficult to conceive how either the sand or the solutions in which the plants grew, or the sand and solutions together, could have absorbed and yielded to the plants more combined nitrogen, either in the form of ammonia, nitrates or otherwise, than would be acquired by the nutritive solutions or a dilute acid solution without plants but otherwise subject to the same conditions.

The natural inferences are that:

(1) No considerable quantity of combined nitrogen was derived from the air and yielded to the plant by the medium in which the plant grew.

(2) The slight loss of nitrates may possibly indicate decomposition, but it is small, varying from 0.8 to 1.3 milligrams, and may very likely be due, in part at least, to experimental errors.

Discussion of Results of Experiments.

The principal statistics of the experiments are collated in the tables in the Appendix to this article, and may be summarised as in Tables 1, 2, 3, 4 and 5, which follow here.

As previously explained, the estimates of the numbers of tubercles were made before the analysis of the plants, and thus the observer was free from bias.

While it is not practicable to give more than a relative idea of

their abundance, this grouping into few, fair number, and large number, presented but little difficulty.

TABLE I.
Experiments with Oats, Series XII, 1889.

SUMMARY OF RESULTS.

	No. of Experiments.	No. of Plants in Experiments.	Average Gain (or Loss —) of Nitrogen.
			Mg.
Not fed nitrogen except in seed.....	4	24	2.3
Fed 304 milligrams nitrogen as calcium and potassium nitrates.....	3	18	—101.5
Fed 607 milligrams nitrogen as calcium and potassium nitrates.....	3	18	—207.8
Total.....	10	60	

Table I epitomises the results with oats. The experiments are arranged in accordance with the amounts of combined nitrogen fed. No tubercles were found upon the roots. It will be noticed that plants not fed with nitrates made a very slight gain (the largest gain was 3.1 and the smallest 1.6 milligrams), while in each case where nitrates were supplied there was a considerable loss, and that the loss increased with the amount of nitrates added. Doubling the nitrogen fed doubled the loss of nitrogen.

TABLE 2.
Experiments with Corn, 1888–1889.

SUMMARY OF RESULTS.

	No. of Experiments.	No. of Plants in Experiments.	Average Gain (or Loss —) of Nitrogen.
			Mg.
Not fed nitrogen except in seed, Series IX, 1888.....	4	7	5.6
Not fed nitrogen except in seed, Series XIII, 1889.....	6	12	9.5
Fed 114 milligrams nitrogen as nitrates, Series IX, 1888.....	4	8	15.6
Fed 607 milligrams nitrogen as nitrates, Series XIII, 1889.....	6	11	— 88.4
Fed 1518 milligrams nitrogen as nitrates, Series XIII, 1889.....	6	12	—236.8
Total.....	26	50	

Table 2 epitomises the results with corn. The experiments are arranged in accordance with the amount of combined nitrogen fed. No tubercles were found upon the roots. It will be noticed that plants not fed with nitrates, and those fed with the smallest proportion of nitrates made a very slight gain, while in the other cases where nitrates were supplied, there was a considerable loss, and that the loss increased with the amount of nitrates added.

TABLE 3.
Experiments with Alfalfa, Series VIII, 1888-1889.

SUMMARY OF RESULTS.

	Root Tubercles.	No. of Experiments.	No. of Plants in Experiments.	Average Gain of Nitrogen.
				Mg.
Not fed with nitrogen except that in seed.....	None.....
	Few.....
	Fair number..	1	3	137.5
	Large number,
	Total.....	1	3	
Fed with 340 milligrams nitrogen as calcium and potassium nitrates.....	None
	Few.....	3	4	84.0
	Fair number..
	Large number,	1	1	382.2
	Total.....	4	5	

Table 3 summarises the results with alfalfa. As explained in Table 10 beyond, the plants made but little growth the first season and a number died. Those which survived made a very satisfactory growth the second season. All the plants had root tubercles.

TABLE 4.
Experiments with Peas.

SUMMARY OF RESULTS.

	Root Tubercles.	No. of Experiments.	No. of Plants in Experiments.	Average Gain (or Loss) of Nitrogen.
Mg.				
CHAMPION OF ENGLAND PEAS. Series VII, 1888.				
Not fed with nitrogen except that in seed.....	None	6	13	—9.8
	Few	1	3	—1.7
	Fair number ..	1	3	85.6
	Large number..	1	3	116.7
	Total.....	9	22	
Fed with 76 to 252 milligrams nitrogen as calcium and potassium nitrates in addition to that in seed.....	None	6	13	—22.7
	Few	4	11	— 3.1
	Fair number ..	3	9	19.7
	Large number..	3	9	49.0
	Total.....	16	42	
Series XI, 1889.				
Not fed with nitrogen except that in seed.....	None	2	6	— 9.0
	Few	1	4	—13.5
	Fair number ..	2	8	69.4
	Large number..	1	4	78.7
	Total.....	6	22	
Fed with 152 to 448 milligrams nitrogen as calcium and potassium nitrates in addition to that in seed.....	None
	Few	2	10	26.5
	Fair number ..	1	4	60.2
	Large number..	7	34	149.6
	Total.....	10	48	
EAST HARTFORD EARLY PEAS. Series X, 1889.				
Not fed with nitrogen except that in seed	None	2	4	—9.6
	Few	5	14	0.1
	Fair number ..	1	4	28.7
	Large number..	8	23	72.9
	Total.....	16	45	
Fed with 76 to 228 milligrams nitrogen as calcium and potassium nitrates in addition to that in seed.....	None
	Few	6	18	—5.6
	Fair number ..	3	11	26.4
	Large number..	8	26	74.5
	Total.....	17	55	

Table 4 summarises the results with peas. The experiments are arranged in accordance with the number of root tubercles observed at the time of harvest.

TABLE 5.
Experiments with Peas and Alfalfa, 1888-1889.

CONDENSED SUMMARY OF RESULTS AND AVERAGES.

Root Tubercles.			Without Nitrogen in Nutritive Solutions.			With Nitrogen in Nutritive Solutions.			Total.		
			No. of Experiments.	No. of Plants in Experiments.	Average Gain (or Loss —) of Nitrogen.	No. of Experiments.	No. of Plants in Experiments.	Average Gain (or Loss —) of Nitrogen.	No. of Experiments.	No. of Plants in Experiments.	Average Gain (or Loss —) of Nitrogen.
					Mg.			Mg.			Mg.
Peas.	{ None	10	23	—9.6	6	13	—22.7	16	36	—14.5	
	{ Few	7	21	—2.1	12	39	0.6	19	60	—0.4	
	{ Fair number.....	4	15	63.3	7	24	28.4	11	39	41.1	
	{ Large number.	10	30	77.9	18	69	99.5	28	99	91.7	
					Mg.			Mg.			Mg.
Alfalfa.	{ None	
	{ Few	3	4	84.0	3	4	84.0	
	{ Fair number.....	1	3	137.5	1	3	137.5	
	{ Large number.....	1	1	382.2	1	1	382.2	

In Table 5 a condensed summary of Tables 3 and 4 is given. The results with Champion of England and East Hartford Early peas are arranged together.

(To be continued.)

THE INTERACTION OF SULPHURETTED HYDROGEN AND THE ORTHOARSENATES OF THE ALKALI METALS.

By LEROY W. McCAY.

Berzelius, to whom we are indebted for the greater part of our information in regard to the sulphur compounds of arsenic, gives two methods for the preparation of the pentasulphide:

1. Saturation of a moderately concentrated solution of arsenic acid with sulphuretted hydrogen; 2. Decomposition in a strong solution, by means of sulphuretted hydrogen, of an alkali arseniate, and precipitation, by the addition of a mineral acid, of the pentasulphide formed.

The action of sulphuretted hydrogen upon arsenic acid I have examined with much care, and, in the preparation of potassium sulphonyarsenate through the action of the gas upon mono-hydrogen potassium arseniate, have obtained results which are in direct opposition to what the statements of Berzelius had led me to expect. It therefore seemed advisable to continue the work and to study the action of sulphuretted hydrogen upon the mono-, di- and tri-alkali arseniates. The results thus obtained prove beyond a doubt that although Berzelius' second method of preparation is in principle correct, yet it is successful only under definite conditions.

The reactions which take place in all three cases are almost identical with those which are characteristic of the action of sulphuretted hydrogen on arsenic acid alone or on alkali arseniates acidified with a mineral acid. The experiments may be classified as follows:

A.—The Action of Sulphuretted Hydrogen on a Solution of Dihydrogen Potassium Arseniate.

1. Sulphuretted hydrogen was passed in a rapid current for eight hours through a saturated solution of the salt. The precipitate formed was found to consist of mono-hydrogen potassium sulphonyarsenate in beautiful crystals, arsenic pentasulphide, arsenic trisulphide and sulphur. The solution, after the removal of the precipitate by filtration, was soon again clouded, and in the fresh precipitate, along with mono-hydrogen potassium sulphonyarsenate, could be readily detected potassium arseniate and arsenite, and free sulphur. Pure arsenic pentasulphide cannot then be prepared by saturating in the ordinary way with sulphuretted hydrogen a *very concentrated* solution of dihydrogen potassium arseniate, and decomposing, through the addition of a mineral acid, the sulphy-salt formed.

2. The foregoing experiment was repeated with a moderately concentrated solution of dihydrogen potassium arseniate, but, with the exception of the failure of the sulphony-salt to crystallise out, the result was the same.

3. (a). 0.9 gram dihydrogen potassium arseniate was dissolved in water and the solution treated in the cold for fifteen hours with sulphuretted hydrogen in a rapid current. The gas, as far as was possible, was kept in large excess all the time. The solution became very yellow and some sulphide separated out, but the greater part of the arsenic remained in combination as a dihydrogen potassium sulpharseniate (?) in a state of semi-solution. A large excess of hydrochloric acid caused the solution to clear rapidly and the arsenic pentasulphide to be precipitated in a flocculent, sulphhydrated form. It was filtered out, washed according to Bunsen's directions (with alcohol and bisulphide of carbon), and weighed in a Gooch crucible, after having been dried at a temperature of 110° C.

Weight of Sulphide found.

0.7661 gram.

Calculated.

0.775 gram.

The filtrate contained sulphyoxyarsenic acid, and the precipitate upon examination gave reactions for arsenic trisulphide.

(b). 0.9 gram of dihydrogen potassium arseniate was dissolved in water and treated with sulphuretted hydrogen, as above described, for twenty hours. The flask containing the solution was provided with a Bunsen valve to keep out the air, but the weight of the sulphide obtained was nevertheless low—0.768 gram. The filtrate contained no sulphyoxyarsenic acid, but the precipitate was mixed with a little trisulphide.

(c). 0.9 gram of the salt was dissolved and treated with sulphuretted hydrogen for twenty hours, all air being carefully excluded by having the escaping gas bubble through water contained in a Volhard-Fresenius absorption apparatus which was attached to the flask containing the solution of the arseniate. The filtrate from the precipitated sulphide was free from sulphyoxyarsenic acid, but the alcohol and bisulphide of carbon washings gave upon evaporation a notable amount of sulphur, and the precipitate itself contained arsenic trisulphide.

(d). 0.9 gram of the salt was put in a two-liter flask, dissolved in water and the solution diluted to about 1900 cm^3 .; the solution was treated with sulphuretted hydrogen in a rapid current until an opalescence appeared. The flask was then filled almost full of cold freshly-boiled water, tightly corked and put away in a cold place for two weeks. Even in this case the formation of the

sulpho-salt was incomplete;¹ only 0.7665 gram of pentasulphide was obtained.

These experiments show that it is impossible to prepare pure arsenic pentasulphide, even from an *ordinary* solution of dihydrogen potassium arseniate, simply by treating the liquid for a long time in the cold with sulphuretted hydrogen in a rapid current.

4. (a). 0.9 gram salt was dissolved in water, the solution diluted to about 500 cm³., heated in a flask to boiling, and treated for eight hours with sulphuretted hydrogen in a rapid current. The heating was then discontinued, but the gas was permitted to flow until the solution had become cold; the flask was then tightly corked and set aside for a day and a night. The pentasulphide thus formed amounted to 0.7758 gram, the theoretical quantity being 0.7750 gram. The washing was very thorough, large quantities of alcohol and bisulphide of carbon being used. By properly diluting, then, the solution of the dihydrogen potassium arseniate and keeping it *hot*, it is possible by Berzelius' second method to prepare pure arsenic pentasulphide. The following mode of procedure proved all that could be desired:

(b). 0.9 gram dihydrogen potassium arseniate was dissolved in water and the solution brought into a bottle, in which it was saturated with sulphuretted hydrogen, and heated under pressure in a manner which I have before described. The solution, at the end of the time, had the same peculiar appearance exhibited by that in experiment 3; the sulphide refused to settle. The addition of strong hydrochloric acid, however, brought about the complete separation of the sulphide, in amount 0.7750 gram; or, calculating as arsenic, 0.3750 gram. These figures coincide with the calculated weights of arsenic pentasulphide and arsenic. The sulphide was evidently pure.

¹ The result of this experiment was so unlooked for that I repeated it, strongly acidifying the solution with hydrochloric acid, however, before saturating with sulphuretted hydrogen, and obtained at the end of the two weeks 0.7746 gram of arsenic pentasulphide instead of the calculated 0.775 gram. In the case of arsenic acid, then, the passage *in the cold* from the oxy-salt through the sulphony-salt to the sulpho-salt takes place slowly, but smoothly and completely, whereas in the case of the corresponding acid salt, when the sulphony stage is reached, there is a partial decomposition into alkali arsenite and sulphur, and that, too, in spite of the presence of an excess of sulphuretted hydrogen.

As will be seen further on, this extraordinary deportment while in the sulphony state is not shown by the two other ortho-salts.

B.—*The Action of Sulphuretted Hydrogen on Hydrogen Dipotassium Arseniate.*

5. To a solution of arsenic acid potassium hydrate¹ was added until the solution possessed a slightly alkaline reaction. Sulphuretted hydrogen was then passed into the liquid until it seemed saturated. After standing twelve hours the solution was decomposed with an excess of sulphuric acid. The precipitate proved to be a mixture of arsenic trisulphide and pentasulphide with sulphur, while the filtrate evidently contained sulphyarsenic acid, arsenic acid and arsenious acid. The large amount of arsenic pentasulphide found was evidence of the formation of considerable sulpharseniate.

6. 100 cm³. of a solution containing 20 grams of pure arsenic acid in 2000 cm³. of water were diluted, rendered faintly alkaline with potassium hydrate, treated for six hours with sulphuretted hydrogen in a rapid stream, and finally decomposed with an excess of hydrochloric acid. The precipitate was washed according to Bunsen's directions, dried at 110° C., and weighed in a Gooch crucible. The sulphide weighed 1.0758 gram, while the theory calls for 1.0913 gram. The filtrate contained small quantities of sulphyarsenic acid, which fact explains the low result.

7. 100 cm³. of the above solution were diluted, made faintly alkaline with potassium hydrate, treated for eighteen hours with sulphuretted hydrogen in a rapid current, and then decomposed with an excess of hydrochloric acid. The precipitate, after proper treatment, weighed 1.0892 gram; calculated weight, 1.0913 gram. The precipitate was therefore practically pure arsenic pentasulphide. The filtrate gave no reactions for sulphyarsenic acid.

8. 100 cm³. of the standard solution, after having been diluted, treated with potassium hydrate until faintly alkaline, heated in a flask upon the water-bath, and treated for three hours with sulphuretted hydrogen, contained all the arsenic in the form of sulpho-salt. The sulphide weighed 1.0913 gram; calculated weight, 1.0913 gram.

9. 100 cm³. of the arsenic acid solution were made faintly alkaline, diluted, saturated with sulphuretted hydrogen, and for one hour heated under pressure in a bottle. Weight of sulphide

¹ I used potassium hydrate, but sodium hydrate or ammonium hydrate will serve the same purpose.

found, 1.0938 gram; calculated weight, 1.0913 gram. This precipitate was also pure pentasulphide. The filtrate was free from sulphonyarsenic acid.

C.—The Action of Sulphuretted Hydrogen on Tripotassium Arseniate.

10. A solution of arsenic acid made strongly alkaline, and treated with sulphuretted hydrogen for a few hours in the cold, showed all the reactions which were noticed in Exp. 6, with the exception that no sulphur separated.

11. 100 cm³. of the standard solution were made strongly alkaline with potassium hydrate, and treated with sulphuretted hydrogen for about eighteen hours. The sulpho-salt alone was formed, and, when decomposed by means of an excess of hydrochloric acid, yielded 1.0925 gram arsenic pentasulphide.

12. 100 cm³. of the standard solution, having been made strongly alkaline, were heated on the water-bath for four or five hours and treated continuously with sulphuretted hydrogen in a rapid current. On addition of hydrochloric acid a precipitate was formed, which, after thorough washing with alcohol and bisulphide of carbon, weighed exactly 1.0913 gram. This is just what the theory demands.

13. 100 cm³. of the arsenic acid solution, having been rendered strongly alkaline by addition of potassium hydrate, treated with excess of sulphuretted hydrogen and heated in a bottle in the water-bath for one hour, gave, after the sulpho-salt had been decomposed with hydrochloric acid, a precipitate which weighed 1.0925 gram. Here also the reaction was complete, all the tripotassium arseniate having been transformed into the corresponding sulpho-salt.

It is therefore true that arsenic pentasulphide can be prepared by saturating an alkali-metal orthoarseniate with sulphuretted hydrogen and decomposing with excess of a mineral acid the sulpho-salt formed, but this process is only complete provided: (1) the solution of the arseniate is properly diluted and kept hot, and the sulphuretted hydrogen passed in excess and for a long time (dihydrogen salt), or, (2) the sulphuretted hydrogen is kept present in such large excess and passed for such length of time that there is no chance for the potassium sulphonyarseniate (which is always formed in passing in the wet way from

arsenic acid to sulpharsenic acid) to split up into potassium arsenite and sulphur, or to escape subsequent complete transformation into the sulpho-salt (di- and tri-alkali salts). This method is admirably adapted for preparing large quantities of arsenic pentasulphide, and that it can be used for the determination of arsenic with a satisfactory degree of accuracy is evident from the results of the quantitative determinations above described.

The results described in this paper will, I think, serve to clear up much of the mystery connected with the subject of the formation of the alkali sulpharsenates in the wet way. The existence, unstable character, and mode of decomposition of sulphyarsenic acid and its salts appear fully capable of accounting for the hitherto seemingly abnormal interaction of sulphuretted hydrogen and the orthoarsenates of the alkali metals.

In conclusion I should say that a number of experiments which I have recently made, have led me seriously to question the accuracy of the views of Berzelius regarding the action of the alkali hydrates on the sulphides of arsenic. I hope before long to be able to speak more definitely of the subject. In the meantime I reserve for myself the right further to investigate the matter.

PRINCETON, N. J., July 1, 1890.

THE INDIAN GRASS OILS.

By F. D. DODGE.

The preparation and properties of citronellic aldehyde, $C_{10}H_{18}O$, the principal constituent of oil of citronella, have been described in a previous paper.¹ A sample of the aldehyde was prepared from thoroughly washed bisulphite compound and redistilled twice. It is a colorless oil, apparently unaltered by light or long standing in a closed vessel, but readily oxidising on exposure to the air.

Its density at 20° is 0.8560.

The observed rotation of the pure substance in a 4-dm. tube, Laurent polarimeter, was $+16^{\circ} 34'$ (mean of 10 observations), whence:

$$[\alpha]_D = +4^{\circ} 50'.$$

¹ This Journal 12, 7.

The index of refraction was determined in the spectroscope, with glass prism of $59^{\circ} 42'$, at 20° C.

$$\begin{array}{ll} \text{Index } (n) \text{ for } H\alpha = 1.442 & \text{for Li line} = 1.4415 \\ H\beta = 1.4515 & \\ H\gamma = 1.4577 & \text{" Na " } = 1.4448; \end{array}$$

whence specific refraction $\frac{n^2 - 1}{(n^2 + 2)d} = 0.3091$, and molecular refraction $R_a = 47.60$.

The calculated refractions are:

1. For the "open-chain" formula, $C_4H_9 - CH=CH - C_3H_6 - COH$, or a similar one:

$$\begin{array}{r} C_{10} = 24.80 \\ H_{18} = 18.72 \\ O \text{ in } >C=O = 2.34 \\ \text{Increment for } -CH=CH- = 1.78 \\ \hline 47.64 \end{array}$$

2. For an aldehyde having a hexatomic nucleus like the menthol series:

$$\begin{array}{r} C_{10} = 24.80 \\ H_{18} = 18.72 \\ O \text{ in } >C=O = 2.34 \\ \hline 45.86 \end{array}$$

There can be little doubt, therefore, that citronellic aldehyde is an open-chain compound and is homologous with acrolein and the aldehydes of the $C_nH_{2n-2}O$ series.

Cymene from Citronellic Aldehyde.

The bromine addition-product of citronellic aldehyde decomposes on heating, as already shown, yielding an oil having the properties of ordinary cymene. From 100 grams of aldehyde, 13 grams of cymene, boiling at 175° – 180° , were obtained. Oxidation with dilute nitric acid afforded a crystalline acid, melting at 177° , which was undoubtedly impure para-toluic acid. By treating citronellic aldehyde with iodine and distilling the product, no cymene was obtained, but a hydrocarbon, boiling near 160° , which has not yet been identified.

Citronellal-phosphoric Acid.

The occurrence of a crystalline compound among the products of the action of phosphoric anhydride on citronellal aldehyde has already been mentioned. The conditions under which this substance was formed were then unknown and several efforts to obtain sufficient for analysis were unsuccessful. Some months later I obtained, from an experiment in which the phosphoric anhydride was added to a cooled solution of the aldehyde in an equal volume of *moist* ether, about two grams of pure substance, which crystallised from alcohol in large transparent prisms and square plates.

This compound is a strong acid, decomposing and dissolving in alkaline carbonates and being reprecipitated on addition of mineral acids.

Analyses gave the following results :

I. Substance, 0.2138 gram ; CO_2 , 0.4009 gram ; H_2O , 0.15695 gram.

II. Substance, 0.1893 gram ; $\text{Mg}_2\text{P}_2\text{O}_7$, 0.0943 gram.

III. Substance, 0.2163 gram ; $\text{Mg}_2\text{P}_2\text{O}_7$, 0.1034 gram.

	Calculated $\text{C}_{10}\text{H}_{19}\text{PO}_4$.	I.	II.	III.
C	51.28	51.13
H	8.11	8.11
P	13.25	...	13.9	13.34

Titration with standard alkali showed that the compound is a monobasic acid, its acid properties being undoubtedly due to a phosphoric group, for the oxidation of the aldehyde group seemed, under the conditions of formation, very improbable. This being the case, the reaction producing the compound is not simply a dehydration, but requires the presence of one or more molecules of water. In fact, in all cases in which any of this acid has been obtained water has been present, the ether used being nearly saturated ; while, if all moisture is carefully excluded and the reaction carried on in a dry benzene solution, no product is obtained.

Although the most favorable conditions for the preparation of this substance have not yet been determined, I have obtained moderate quantities by the following process :

5 grams phosphoric anhydride are covered with 20 cc. dry benzene ; the necessary amount of water (1 molecule) is now added,

dissolved in ether, *i. e.* 31 cc. saturated ether. The vessel is kept as cool as possible. A cake of metaphosphoric acid forms and the greater part of the liquid is then poured off, 10 grams aldehyde (or, equally well, 20 grams citronella oil) slowly added and the whole well mixed. The vessel is allowed to stand at 70° several hours. Concentrated sodium carbonate is then added until the solution is alkaline, the excess of oil separated, and the aqueous solution (kept as concentrated as possible) is extracted with ether until colorless. If it is still colored a few drops of hydrochloric acid are added and the solution again extracted, this cautious acidifying being repeated till the liquid, after extraction, is perfectly colorless. An acid by-product seems to be formed in the reaction, which is precipitated by hydrochloric acid before the phosphoric derivative. Excess of concentrated hydrochloric acid is now added, the solution chilled and filtered, and the precipitated acid crystallised from warm dilute alcohol.

The alcoholic solution should be colorless; if much oil is present it can be removed by fractional precipitation with water or by washing the crystals of the acid with dry ether. The yield of acid is about two grams.

The solution from which the acid has been thrown down by hydrochloric acid will generally afford more product on concentration. Much of it, however, is decomposed by the continued action of the hot water, with formation of an oil. In some cases I have noticed the separation of long needles from this solution. These melt at 180° and are readily volatile; their nature is not yet ascertained. Ordinary glacial phosphoric acid does not answer for the preparation of this compound; I have obtained it only by the use of phosphoric anhydride and water.

Properties.—It is sparingly soluble in water, readily in alcohol, with difficulty in ether. Its crystalline form varies: from alcohol, or ether-alcohol, and generally by slow crystallisation, it forms square plates; from dilute alcohol, and sometimes from water, prisms or long flat needles are obtained. Its system is not yet determined. It melts near 203°. It is moderately stable in the presence of aqueous acids, but warm alkalis decompose it with formation of oil. As already shown it is a monobasic acid. The potassium salt is very soluble and crystallises in long needles; the sodium salt crystallises more readily and in forms resembling those of the free acid. The ammonium salt resembles the potassium salt.

Aniline citronellal-phosphate is readily obtained by adding aniline in slight excess to an alcoholic solution of the acid. Ether precipitates the salt in white needles melting at 165° . The quinoline salt also crystallises in needles. As was to be expected, citronellal-phosphoric acid is optically active. A solution of 5.84 grams in 100 cc. of 95 per cent. alcohol showed a rotation in a 2-dm. tube of $+2^{\circ} 58'$. I have not succeeded in determining whether the crystallised acid is also active. As is well known, there are but few substances which are rotatory both in solution and in the crystalline form.

Constitution.—The most obvious formula for citronellal-phosphoric acid is

$$\text{C}_9\text{H}_{17} - \text{CH} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{PO} - \text{OH},$$

which expresses the fact, among others, that in the aldehyde the group $-\text{COH}$ alone takes part in the reaction. Evidence on this point is afforded by the fact that the solution of the sodium salt of the acid does not reduce ammoniacal silver solution even on boiling. If this supposition be true, there is no apparent reason why other aldehydes should not react similarly. In the literature of aldehydes, however, no mention is found of such phosphoric derivatives. An analogous body may be the crystalline compound of cinnamic aldehyde with nitric acid, discovered by Dumas and Peligot.¹ I have made a series of experiments in the endeavor to prepare phosphoric derivatives of other aldehydes, as yet unsuccessfully. No such compound could be obtained from cinnamic aldehyde, benzaldehyde, chloral, cenanthol, or citriodoric aldehyde (the constituent of lemon grass oil below described). This work, however, is not yet finished.

The action of heat on citronellal-phosphoric acid and its salts, and its oxidation and reduction products, will be reserved for a subsequent paper.

Lemon Grass Oil.

The uncertain botanical origin of this oil, its similarity in properties to citronella oil, and the fact that its principal constituent is a peculiar aldehyde, have been noted in the first paper (l. c.). With the assistance of Mr. Geo. A. Ferguson, a student in this laboratory, I have been enabled to investigate the oil more closely. The sample used was a Ceylon oil, redistilled in this city. It has a light yellow color and possesses the very characteristic odor of

¹ Ann. Chem. (Liebig) **100**, 104.

the lemon verbena. The specific gravity at 22° is 0.886; at 15.5°, 0.8955.

On distillation the oil boils between 200° and 240°, a small residue being not volatile at the latter temperature. The principal fraction was from 220°–225°. The oil appears to suffer less alteration or to be more homogeneous than citronella oil, which may be due to its recent redistillation. No indications of the presence of mineral oil or paraffins were observed. The reactions of the oil with ammoniacal silver solution, with phenylhydrazine, and with acetyl chloride, are the same as with citronella oil. With sodium bisulphite, however, its behavior is quite different, and, as far as I am aware, unique.

Isolation of the Aldehyde.

In the earlier experiments we proceeded exactly as with citronella oil. 150 grams bisulphite, in saturated solution, were added to 200 cc. oil. A white magma was obtained, which was pressed and washed with ether. The dry precipitate was mixed with crystallised sodium carbonate and the aldehyde distilled off in a current of steam. When an excess of oil is used the reaction proceeds as in the case of citronella, but when the amount of bisulphite is increased a different result is obtained and the isolation of the aldehyde becomes simplified. The following process we have found most convenient: 1000 grams dry bisulphite are dissolved in 5 liters hot water; while still slightly warm, 1 liter oil is added at once. The mixture is vigorously stirred for several minutes; it soon becomes very warm, and a pasty mass of bisulphite compound results. After two or three hours, however, the precipitate will have entirely redissolved, leaving a heavy solution, containing the aldehyde, and a layer of residual oil (300 cc.) above. In 24 hours the solution is perfectly clear and may be siphoned off and filtered.

Concentrated sodium hydrate is added to the filtered solution until strongly alkaline, and, after 24 hours, the supernatant layer of liberated aldehyde is separated, filtered and dried.

The product is a yellow oil of very pleasant citrine odor. The yield reaches 65–68 per cent. of oil employed. Redistillation with steam lightens the color; it distills very slowly and we have not yet obtained it colorless. We were unable to detect any difference in properties between this oil and that obtained from the solid bisulphite compound.

The aqueous liquid containing the aldehyde has curious properties. It may be concentrated at 100° without apparent alteration, becoming more and more viscid until its density reaches 1.4, when on cooling it becomes supersaturated, and slight agitation, rubbing with a glass rod, etc., will cause immediate solidification. By cautious evaporation we have, in one case, obtained transparent crystals an inch in length, whose analysis will be given later. It is evident that in this solution we are not dealing with a typical bisulphite solution, as in the case of vanillin, or phenanthrenequinone, for the aldehyde is not set free by acids. On adding to this liquid an equal volume of concentrated hydrochloric acid the result is a thick precipitate of salt, while the aldehyde remains in solution. Barium chloride produces an abundant precipitate of sulphite and sulphate. By removing excess of barium with sodium carbonate and filtering, a liquid is obtained, which may be concentrated as before and still contains the aldehyde. If a little sulphuric acid is added it can no longer be concentrated, but darkens on heating and liberates sulphurous acid. Caustic alkalies, however, instantly set free the aldehyde. If this liquid were merely a solution of a typical bisulphite compound in excess of bisulphite, further addition of aldehyde should cause the whole to precipitate. This does not occur; the solution seems to be without effect on the aldehyde.

All the observed facts indicate the presence of a curious combination of aldehyde, sulphurous acid and soda—most probably a complex one, for the concentrated solution diffuses very slowly, behaving in fact somewhat like a gelatine solution.

The analysis of the above-mentioned crystals also points to a complicated formula :

5.0026 grams lost at 100° 2.650 grams H₂O, or 52.9 per cent.

Na in dry salt = 27.6 per cent.

S " " " = 22.48

The tentative formula C₁₀H₁₆O.2NaHSO₃.4Na₂SO₃.50H₂O requires—

H₂O 52. per cent.

Na in dry substance 27.1

S " " 22.6

The analyses will be repeated on fresh material. On heating these crystals they readily fuse in the crystal water—the latter is almost entirely lost by standing over sulphuric acid. Further

heating liberates the organic portion in fumes which resemble the aldehyde in odor, and the residue appears to be entirely sodium sulphite.

Properties.—This substance is a light yellow liquid, with an odor like that of the original oil, but less penetrating. Its density at 15.5° is 0.8968. It begins to boil near 225°, with gradual decomposition or alteration. Analysis :

	Calculated for $C_{10}H_{10}O$.	Found.
C	78.94	78.79
H	10.52	10.82

The aldehyde is then isomeric with camphor, and, from its most evident property, we propose for it the name *citriodoric aldehyde*. Vapor density determinations have not as yet given concordant results. In a 1-dm. tube a rotation of $+1^{\circ}30'$ was observed, but the sample was not colorless and the result is uncertain. Consideration of the possible formulæ of this substance indicates that it is probably inactive.

Owing to the instability of the bromine addition product we were unable to determine the unsaturation by titration. Determination of the molecular refraction has not given a satisfactory result, owing to the lack of a perfectly pure specimen; the dispersion is much greater than in the case of citronellic aldehyde.

With silver solution, phenylhydrazine, aniline, and paratoluidine, the behavior of the aldehyde is like that of citronellic aldehyde.

Action of Dehydrating Agents.

Citriodoric aldehyde, being isomeric with camphor, should yield on dehydration para-cymene or one of its isomers. Such, under certain conditions, is the case. By the action of phosphoric anhydride on the aldehyde dissolved in 10 parts of ether, the temperature being kept low, no cymene or light oil is obtained, but there results an oil of offensive odor, boiling at 200°–260°, and a fluorescent substance not volatile at 260°. Semmler¹ also noticed among the products of the action of phosphoric anhydride on geraniol a poly-terpene which showed beautiful dichroism. By direct action of phosphoric anhydride (50 grams) on the aldehyde (25 grams), a distillate of 6 grams was obtained, passing over between 170° and 200°. This possessed the odor of cymene, and was identified as *para*-methyl-propyl-benzene by oxidation

¹Ber. d. chem. Ges. 23, 1093.

with excess of hot permanganate and conversion of the resulting insoluble acid into the characteristic crystals of methyl terephthalate, melting at 140° .

Zinc chloride does not appear to produce cymene. Concentrated hydrochloric acid acts very readily on the aldehyde, with evolution of heat. The product is a dark red oil, from which, by distillation with steam, cymene is readily separated, the yield reaching 50 per cent. The residue is a dark viscid product of peculiar odor. The cymene is the ordinary modification, as was shown by conversion into para-toluic acid, melting at 180° . This simple transformation of a probably "open-chain" compound into an aromatic hydrocarbon is remarkable.

Reactions.—By treatment with zinc dust in acetic acid solution a product was obtained which probably contains the corresponding alcohol. It has a peculiar odor, is decomposed on distillation, and has not yet been purified.

Oxidation by dilute permanganate affords a mixture of acids. Neither acetic nor valeric acid was detected.

Alcoholic ammonia reacts with the aldehyde at 150° – 170° , with formation of an unstable product, not yet identified.

The oxime was obtained as an aromatic oil which could not be induced to crystallise.

Constitution.—As yet we have few facts on which to construct a formula for this compound. The formation of para-cymene by simple condensation establishes, as in the case of citronellaldehyde, the presence and position of a methyl and a propyl group. It seems probable also that the aldehyde is a fatty derivative with two ethylenic bonds. Whether it is the aldehyde corresponding to geraniol (see below) or not, it is impossible as yet to say.

Residual Oil.

The portion of lemon grass oil, which does not combine with bisulphite, was fractioned. We obtained indications of the presence of a terpene, but the oil alters very rapidly on distillation. It seems probable also that cymene is present in the oil, as it would easily result from condensation of the aldehyde.

Indian Geranium Oil.

The oil obtained from *Andropogon schoenanthus* L. has been known as: Rusa, Row-sah, Rosa, Rosé, or Roisa oil; oil of

Namur, Nimar, Namar or Namaur; Khandesh oil, Palmarosa oil; ginger-grass, Indian or Turkish geranium oil; Ingweröl; and also by many native names. Oils of ginger-grass and Turkish geranium are distinct commercially and have different market values. There is little doubt, however, that they represent different qualities of the same oil.

Stenhouse¹ and Gladstone² examined oils supposed to be the one in question, but the first insight into the nature of the geranium oil is due to Jacobsen,³ who found the principal constituent to be a substance boiling at $232-3^{\circ}$, to which he assigned the name *geraniol*.

Geraniol has the composition $C_{10}H_{18}O$ and is isomeric with borneol, cineol, and menthone. It is a colorless, strongly refractive liquid, of peculiar, rose-like odor; it is miscible with alcohol and ether, and insoluble in water; it does not solidify at -15° ; its boiling point is higher than that of any of its isomers, and it is optically inactive. On exposure to the air it is very gradually altered, absorbing oxygen and becoming a thick, viscid mass. The density of geraniol at 15° was 0.8851; at 21° , 0.8813. Fusion with potash, digestion with barium hydrate, or oxidation with permanganate yields iso-valeric acid. Distillation with phosphoric anhydride or zinc chloride produces a terpene, *geraniene*, $C_{10}H_{16}$.

Geraniol readily absorbs hydrochloric acid gas, with formation of a compound analogous to bornyl chloride. In fact it resembles borneol in most of its reactions and is probably a monatomic alcohol. The physical difference, that it is liquid and inactive, is true of nearly all its derivatives. Geranyl chloride, $C_{10}H_{17}Cl$, is a yellow oil, of peculiar aromatic odor. It does not solidify at -15° , and decomposes on heating. Various ethers of geraniol have been prepared from the chloride by reaction with potassium salts. Geraniene, $C_{10}H_{16}$, boils at $162^{\circ}-164^{\circ}$, and is inactive; it forms a liquid hydrochloride, but no hydrate, when treated by Wiggers' method.

I have examined several samples supposed to be Indian geranium oil. One specimen was found to behave exactly as Stenhouse has described. About one-half of the oil distilled below 180° , leaving a viscid residue. No portion corresponding to geraniol was obtained. The distillate consists probably of a

¹ J. Chem. Soc. 1844, 122.

² Ibid. 1864, 10.

³ Ann. Chem. (Liebig) 157, 232.

terpene or terpenes. Not being confident that this was genuine oil I made no further examination of it.

A sample of ginger-grass oil from Ceylon gave better results; it seemed to be the oil described by Jacobsen. On distillation it passed over between 150° and 260° , leaving considerable residue. The portion between 100° and 170° contained water and ordinary alcohol. The principal fraction was 227° – 233° ; which possessed the properties ascribed to geraniol.

This product shows great similarity to the substance isolated from citronella oil and termed provisionally "citronellyl alcohol."

The latter, however, boiled some 10° lower, which might be due to admixed terpene, and further purification was desirable.

Haller¹ has shown that camphor and borneol may be separated by treatment with a dibasic acid. Borneol, being an alcohol, forms an acid ether which is soluble in alkalis. It seemed probable that this process could be applied for the purification of the desired alcohol.

16 grams of "citronellyl alcohol," boiling at 222° , were heated with 13 grams of succinic acid in a tube, at 140° to 180° , for fifty hours. The contents of the tube were washed with ether, the ether solution extracted with potassium carbonate solution, and the latter, again, extracted with ether to remove traces of oil. The alkaline solution was then heated with dilute caustic potash and the liberated oil collected and fractioned. It was found to boil at 225° – 230° and possessed a faint odor of roses.

Analysis gave an unsatisfactory result:

	Calculated.		
	$C_{10}H_{20}O$.	$C_{10}H_{18}O$.	Found.
C	76.92	77.92	75.96
H	12.82	11.70	12.79

Geraniol, treated in this way, gave a very similar product, which was unfortunately lost before an analysis was made.

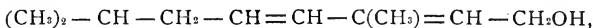
My work had reached this point when an investigation of Indian geranium oil, by F. W. Semmler, was published.² He has confirmed Jacobsen's results and has shown that geraniol has the composition $C_{10}H_{18}O$, and that the molecular refraction indicates the presence of *two* "ethylenic" bonds. Hence a ring structure is inadmissible (as in the case of citronellic aldehyde), and geraniol must be classified with the "open-chain" unsaturated alcohols, $C_nH_{2n-2}O$.

¹ Compt. rend. 108, 1308.

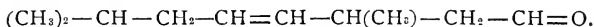
² Ber. d. chem. Ges. 23, 1098.

Cautious oxidation of geraniol by permanganate yields valeric acid in nearly molecular quantity.

From these facts he deduces as the most probable structure of geraniol :



according to which it should be inactive, and very closely related to the active citronellic aldehyde, whose provisional formula has been given as :



As Herr Semmler has expressed his intention of continuing his work, I have given up further experiments on this oil. When in possession of more material, however, I hope to solve the question of the identity of geraniol with "citronellyl alcohol."

In reviewing the results thus far obtained in the study of the grass oils a few general facts become apparent. The constituents of the oils belong to the unstudied group of compounds which have an open-chain structure and readily suffer condensation, yielding terpenes, para-cymene, or derivatives of the latter.

This group is quite probably a large one, but as yet citronellic and citriodoric aldehydes and geraniol are the only members whose structure is even approximately known. The alcohol, $\text{C}_{10}\text{H}_{18}\text{O}$, and aldehyde, $\text{C}_{10}\text{H}_{16}\text{O}$, found by Bruylants¹ in oil of tansy, doubtless fall also in this group.

Isomeric with geraniol and citronellic aldehyde are borneol, cineol, terpineol and menthone, all of which have a six-atom nucleus, while of the ten or more substances having the composition $\text{C}_{10}\text{H}_{16}\text{O}$, camphor is the only one whose structure is known, this also having a six-carbon ring.

It is remarkable that the two aldehydes found in citronella and lemon-grass oils differ from all known aldehydes in two peculiar properties; the first, in forming citronellal-phosphoric acid, the second, in yielding the stable bisulphite solution.

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¹ Ber. d. chem. Ges. **11**, 449.

THE CO-EFFICIENT OF MINERAL CONDENSATION IN CHEMISTRY.

BY T. STERRY HUNT.

§1. That the solid and liquid mineral species known to us (including under the designation of minerals all distinct forms of unorganized matter) are formed by a process of intrinsic condensation or so-called polymerisation from simpler chemical species, which are themselves often gaseous, and, moreover, that this condensation is very considerable, is a conclusion to which chemists have been naturally led. The problem of fixing its amount, or, in other words, of determining the co-efficient of the condensation which results in the production of such mineral species, is one which must present itself to every earnest student of chemical physics, but has nevertheless hitherto been generally disregarded. A reason for this neglect of the problem is to be found in the belief that it does not admit of solution, as may be shown by citations from the writings of many eminent chemists.

§2. Thus Wolcott Gibbs in 1877, after reviewing the researches of his predecessors, Marignac, Scheibler, H. Deville and Debray, on the various polytungstates and polymolybdates, and his own important contributions to the subject, describes these various bodies as salts of "complex inorganic acids," and proceeds to illustrate by formulas the results of their chemical analysis. Of a certain hydrated phosphovanadotungstate of barium examined by him he declares that "it has the highest molecular weight yet observed, 20,058." By this we are to understand no more than that this number corresponds to the simplest chemical formula admissible, for he further says, "We have no positive knowledge of the composition of these salts, their molecular weights being, as in the case of most inorganic compounds, entirely unknown," adding that research "tends constantly to show that the structure of inorganic bodies is more complex than was formerly supposed." The language of Roscoe in 1884 embodies the same thought when he speaks of looking forward to "the establishment of a systematic inorganic chemistry which need not fear comparison with the organic branch of our science"; and adds, referring to the complex inorganic acids of Gibbs: "It is well to be reminded that

¹ Gibbs: *Complex Inorganic Acids*, *Am. J. Sci.* (3) **14**, 61.

complexity of constitution is not the sole prerogative of the carbon-compounds, and that before this systematisation of inorganic chemistry can be effected we shall have to come to terms with many compounds concerning whose composition we are as yet wholly in ignorance."¹ It may be remarked, in passing, that the retention by these writers of the old antithesis between organic and inorganic chemistry, as distinguishing carbonaceous compounds from other species, can only serve to hinder the systematisation and the unification of the facts of the science.

Still more recently, in 1889, Victor Meyer, in his address before the Association of German Naturalists and Physicians at Heidelberg on The Chemical Problems of To-day, says with regard to the question of intrinsic condensation: "We know to-day very well that the silicon oxide cannot have the formula SiO_2 , and that this must be multiplied by a very large factor, but of the numerical value of this last we have no indication." Further he adds: "We lack the least knowledge in regard to the true molecular weight of minerals."²

§3. The direct and concise language of Louis Henry of Louvain, in 1879, may be taken as a fuller expression of the opinions generally entertained by chemists on this subject up to the present time. Having shown that for most oxides of the elements the normal forms corresponding with the chlorides, as in the case of iron, aluminum, titanium, silicon, etc., are unknown, and that we possess only greatly condensed polymers of these oxides $(\text{RO}_x)_n$, he proceeds to inquire: "What is the true value of n , the co-efficient of polymerisation, or, in other words, what is the real molecular formula of these polymeric oxides? These questions are doubtless of great interest, but it should be stated at once that it is absolutely impossible to give a direct answer. I do not know of any fact which would allow us to assign an absolute value to the co-efficient of polymerisation, n So far as facts will permit a conclusion, we may affirm that in most cases this number is very high, though different for different oxides."³

¹ Roscoe: Address to the Chemical Section of the Brit. Assoc. Adv. Science, at Montreal in 1884; Report, p. 663.

² Deutsche Rundschau, Nov. 1889; translated by L. H. Friedberg in the J. Am. Chem. Soc. **11**, 101.

³ Louis Henry: Etudes de Chimie Moleculaire, Part I; Les Oxides Metalliques, Ann. Soc. Scient. Brux. 1879. A translation of this, by Prof. T. Carnelley, entitled "The Polymerisation of Metallic Oxides," appears in the L. E. and D. Philos., May and August, 1885. See farther the author's "New Basis for Chemistry," pp. 117-122; also *ibid.*, 2d ed., p. 217, note.

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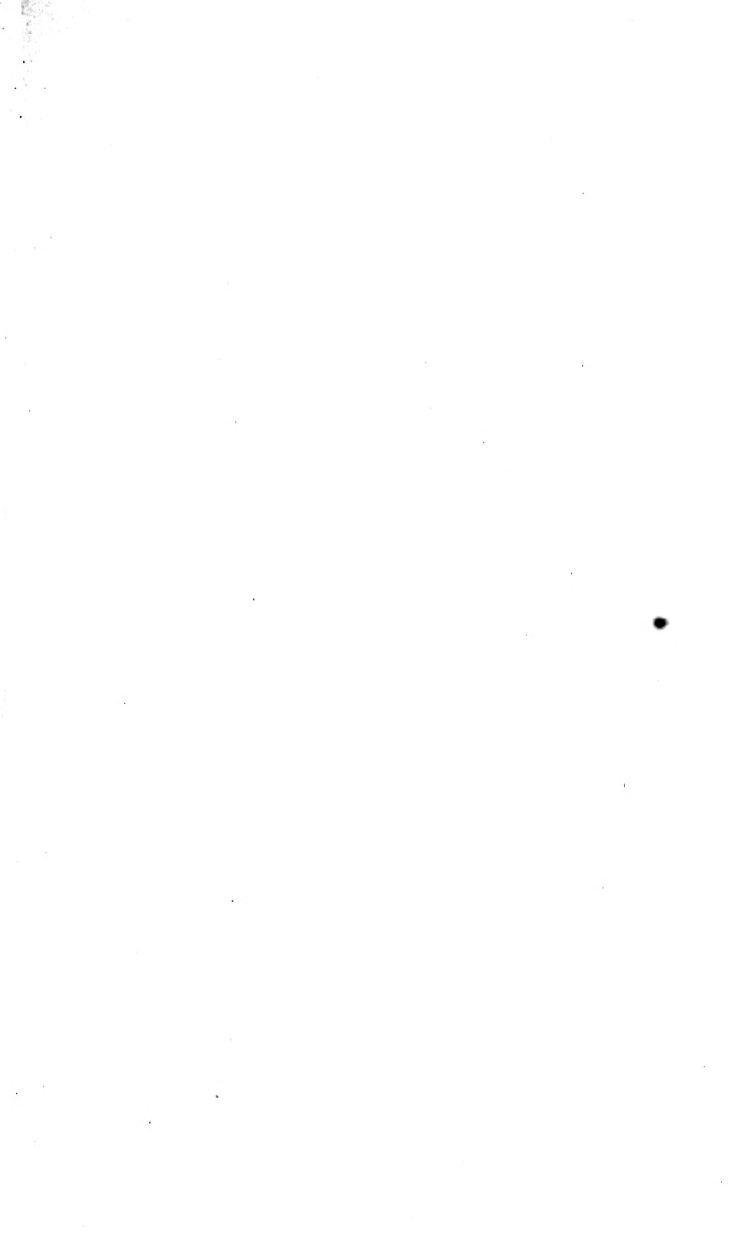
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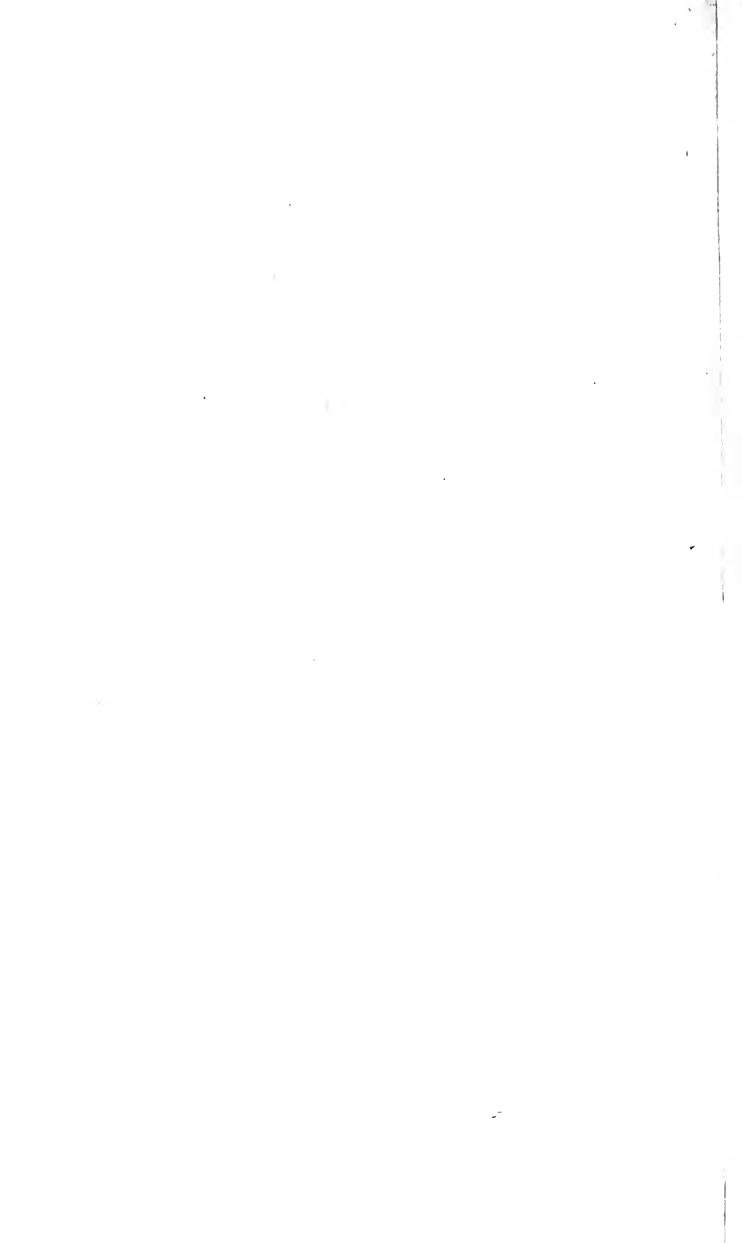
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§4. The same important questions had been propounded by the present writer in 1853, when, after noting that the equivalent weights for volatile bodies are known from the densities of their vapor, but in the case of non-volatile bodies are assumed, it was said that "having determined the true equivalent of a species from the density of its vapor, the inquiry arises whether a definite and constant relation may not be discovered between its vapor-density and the specific gravity of a species in its solid state. Such a relation being established, and the value of the condensation in passing from a gaseous to a solid state being known, the equivalents of solids, like those of vapors, might be determined from their specific gravities." The question was then asked, "What is the value of the condensation which takes place in the change from the gaseous to the solid state? or, in other words, what equivalent corresponds to a given specific gravity in any crystalline solid?" It was further said: "The equivalent of a crystallised species may often be a multiple of that deduced from those chemical changes which commence only with the destruction of its crystalline individuality." This point was then illustrated by examples in the history of various soluble crystalline species.¹

§5. The question thus proposed by the writer in 1853, and repeated by Louis Henry in 1879, was persistently kept in view by the writer, and discussed at intervals in many published papers until 1886, when he arrived at what he has elsewhere put forth as, in his opinion, a simple and natural solution. This is found in the conclusion that the volume not only of gases and vapors but of all species, whether gaseous, liquid or solid, is constant, and that the integral weight—being the so-called equivalent or molecular weight—varies directly as the density, for which he proposes as the unit that of hydrogen at the standard temperature and pressure of 0° and 760 mm.

In all cases of polymerisation and depolymerisation of gases and vapor, or, in other words, of intrinsic condensation and intrinsic expansion at ordinary pressure, the law of volumes, so far as known, holds good; that is to say, these changes are subordinate to a simple ratio of volumes. This same law, it is here maintained, applies

¹ "The Theory of Chemical Changes and Equivalent Volumes," *Am. J. Sci.*, March, 1853 (15, 226-234); also in *L. E. and D. Philos.* (4) 5, 526; and in a German translation in the *Chem. Centrbl.* 1853 (p. 349). This paper is reprinted in the author's *Chem. and Geol. Essays* (1874), pp. 426-437. See also "A New Basis for Chemistry," Chap. IV.

equally to the production of dense vapors of liquids under increased pressure at temperatures above their critical points. Such dense vapors are polymers, which, on reduction of temperature, pass into liquid or solid polymers; the law of condensation by volumes being, by the present hypothesis, assumed to be a universal one. The relations here indicated have been elsewhere considered at length, when, after discussing the law of volumes in ordinary cases of condensation or polymerisation, it was said: "All analogy leads us to extend this law to the still greater condensations observed in the dense vapors into which liquid species above their critical points are resolvable, and to the farther condensation of these vapors into liquid and solid forms—to assume, in fact, that the law of combination by volume, like that of combination by weight (with which, so far as experience shows, it is indissolubly linked), is universal." If this assumption, which appears to be in accordance with all the facts known, be admitted, the great problem proposed, namely, the fixing of the co-efficients of condensation for liquid and solid species, though a complex one, is solved.

§6. As a preliminary to a further treatment of this problem it here becomes important to note the relations between what (§1) we have designated respectively as the "chemical species" and the "mineral species." This will, moreover, serve to explain the language used in 1853, and cited above in speaking of crystalline species, as to "those chemical changes which commence only with the destruction of crystalline individuality." We may perhaps best approach the subject by conceiving the characters of a given species to be imposed upon matter by a force which is the form of that species, and which makes it what it is. The permanence of what we recognise as elementary species, in opposition to the notion of their transmutability, is the foundation of our chemical science, and from this it follows that secondary forms are imposed upon these, and present an ascending series; often passing through two or more chemical forms before receiving the mineral form, which may be in turn subordinated to some biotic form.

§7. These relations may be illustrated by well-known chemical facts: acetic and formic aldehydes and their sulphur and chlorine derivatives present many instructive cases of polymerism available

¹ See "A New Basis for Chemistry," in several chapters, and further in chap. XIV of the 2d ed. thereof. Also in an essay on "The Foundations of Chemistry," §15-19, *This Jour.* **10**, 344, from which the above extract is taken, and *Chem. News* **58**, 193, 205, 212.

for our purpose. Thus acetaldehyde, itself a very light and volatile liquid, is readily transformed into a denser and less volatile species, paraldehyde, which becomes a crystalline solid at 0° , melting at 10° , and having a vapor-density equal to $3(\text{C}_2\text{H}_4\text{O})$, or three times that of the normal aldehyde, into which, however, it is easily changed. The same aldehyde also gives a less fusible crystalline polymer, metaldehyde, the integral weight of which, from the facility with which it reverts without melting to the normal vaporous aldehyde, is unknown. Again, formaldehyde is a gas soluble in water, from which by heat it is in part expelled and in part changed into a white volatile, crystalline solid insoluble in water, alcohol or ether, melting at 152° , but passing at a lower temperature into a gas having the density of the normal formaldehyde. A similar change is also effected when it is heated with water under pressure to a temperature above 100° , the normal aldehyde being taken into solution. This insoluble body, which is sometimes called methylene-oxide, and yields another and a less fusible modification, has been regarded as $3(\text{CH}_2\text{O})$, but its integral weight is uncertain. When a solution of formaldehyde is digested with milk of lime it is changed into a sugar which has been named formose, represented by the general formula of the glucoses, $\text{C}_6\text{H}_{12}\text{O}_6 = 6(\text{CH}_2\text{O})$. Indeed, by modifying the conditions of experiment many species of sugar, alike non-fermentescible and fermentescible, are obtained from formic aldehyde. From one of the latter, which has been designated acrose, and is a form of levulose, it has been found possible to produce anhydrous crystalline dextrose, and thus from the formic aldehyde itself to effect the synthesis of dextrose.¹

§8. Other striking examples alike of isomerism and of polymerism are seen in many hydrocarbons, as in the terpenes, in acetylene and amylenes; while the higher olefines are all polymers and possible homologues of the as yet unknown methylene CH_2 . In the case of the terpenes proper we have a large number of distinct liquid and solid species differing alike in boiling point, in optical characteristics, and in various chemical relations, but having a common vapor-density corresponding to $\text{C}_{10}\text{H}_{16}$. These include (1) pinenes, which are liquids boiling at 156° – 160° and having a specific gravity of about 0.876 at 0° ; (2) citrenes; (3) sylvestrene; (4) terpinele; all liquids boiling from 170° to 176°

¹Fischer: *Ber. d. chem. Ges.* **23**, 372, cited in *This Journal* **12**, 357–364.

and with specific gravities very near that of the pinenes; while the (5) camphenes are solid crystalline species. The various pinenes and citrenes are in great part broken up by heat into pentene, C_5H_8 , which is again convertible into terpine. The various terpenes are, moreover, easily polymerised, yielding denser and less volatile liquids, including sesquiterpenes, $C_{15}H_{24}$, and still higher polymers boiling at 300° and upwards. Acetylene, C_2H_2 , under proper conditions of temperature, gives rise to a number of polymers, of which it suffices to mention benzene, $3(C_2H_2)$, cinnamene, $4(C_2H_2)$ (itself a liquid passing into a solid modification), and retene, $9(C_2H_2)$, a crystalline solid. Of the higher olefines, at least three are known as solids at ordinary temperatures, namely, octodecylene, $18(CH_2)$, cerotene, $27(CH_2)$, and melene, $30(CH_2)$, having melting-points of from 18° to 62° and specific gravities of 0.79, 0.86 and 0.89, respectively, water being 1.00. The integral or so-called molecular weight of these various hydrocarbons is known by the density of their vapors, as in the similar cases of the chlorides of carbon, silicon, aluminum and iron, and of the volatile oxides like those of carbon, arsenic, sulphur, selenium, ruthenium and osmium.

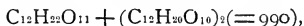
§9. By far the greater number of species, however, are either fixed at high temperatures or undergo heterogeneous decomposition thereby, and may be divided into two categories. First, those which are soluble in water or some other liquid, from which they can be recovered unaltered by change of temperature or by evaporation of the solvent. Such are the sugars and a vast number of non-volatile hydrocarbonaceous species, a great many chlorides, sulphates, phosphates, carbonates and other salts, as also the elementary solid species, sulphur, phosphorus and iodine. For these various bodies water, alcohol, ether, benzene, acetic acid, carbon disulphide and other solvents are familiarly employed. In the second category is included the great number of species which are altogether insoluble, or else are either decomposed, or enter into more or less stable combinations with their solvents. Such are the native silicates, oxides, carbonates and sulphides among compounds, and the various metals among elementary species.

§10. For these two categories of bodies it is obvious that the question of their integral or molecular weight must be approached by a wholly different process from that applied to volatile

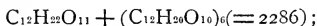
bodies. Much attention has of late been given to the cryoscopic method of Raoult (with its modifications), which is applied for fixing this value for soluble non-volatile species, and depends upon the reduction of the temperature of congelation of the solvent which takes place after the solution therein of a known proportion of the solid species to be examined; the dissolving liquids chiefly used hitherto being water, acetic acid and benzene. The results obtained are approximative, and, moreover, are extremely instructive as illustrations of the subject now under consideration. Thus, Tollens and Mayer have deduced thereby for formaldehyde (obtained in aqueous solution by effecting the transformation of the insoluble formic paraldehyde by heating it in a sealed tube with water to near 140°) the numbers 34 and 35, the calculated integral or molecular weight being $30(=CH_2O)$. This solution, heated in a water-bath, regenerates the insoluble polymer, but evaporated over sulphuric acid gives a soft, soluble solid which, by Raoult's method, is found to correspond to $2(CH_2O)$. By applying this same method to dextrose, these observers found the number 188.7, the received formula for this and the other true glucoses being $C_6H_{12}O_6(=180)$; while arabinose and its isomer xylose, represented by $C_5H_{10}O_5(=150)$, give the numbers 155.1 and 154.1. For cane sugar and for lactose, which, with many other sugars, belong to the diglucosic type, designated as saccharose and represented by $C_{12}H_{22}O_{11}(=342)$, they found, by the method of Raoult, numbers which sustain this formula. For the sugar named raffinose, which occurs with saccharose in certain syrups, three formulas, with C_6 , C_{12} and C_{18} respectively, have been proposed. The latter, making it a triglucosic sugar, is $C_{18}H_{32}O_{16.5}H_2O(=594)$, and experiments by the cryoscopic method gave numbers from 544 to 644, thus sustaining the triglucosic character, and showing at the same time that the range of error due to the necessary imperfections of the process is not inconsiderable.

§11. The recent application of this method to various uncrystalline amyloid bodies has given further results of great interest. The studies by many investigators of the hydrolysis of starch had already led to the conclusion that its constitution is far more complex than is indicated by the ancient formula $C_6H_{10}O_5$. The first action of cold dilute acids thereon changes it into the so-called soluble starch, which by hydrolysis is slowly converted into

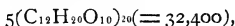
amylodextrine, with the production of a portion of dextrose. The action of diastase, in like manner, by successive stages in hydrolysis gives rise to maltose and other forms of dextrine. By Raoult's method maltodextrine gives numbers closely approximating



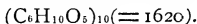
and amylodextrine,



inulin having a composition intermediate between the two. Raoult's method could not be applied to starch paste, but with soluble starch the depression in temperature produced, though slight, corresponded in a number of experiments to integral weights varying from 20,000 to 30,000. Messrs. Brown and Morris, to whom we owe these late investigations, are led to assign to soluble starch the formula



thus multiplying the old empirical formula $C_6H_{10}O_5$ by 200. By the author's hypothesis, however, as restated in §5 of the present paper, the highest integral weights compatible with the observed specific gravities of starch and other amyloid bodies are approximately 32,000, and it therefore seems probable that the so-called soluble starch, which is apparently the first product of the depolymerisation of true starch, should be represented by some simple fraction, perhaps one-half the above, leading to an integral weight for soluble starch of 16,200. The above formula of Brown and Morris, equal to $200(C_6H_{10}O_5)$, will then represent starch itself, with an integral weight of 32,360 ($O = 15.96$) and a theoretical specific gravity of 1.509. The recent examination by Sabanéeff of glycogen by Raoult's method leads to the formula



§12. It will now be sufficiently evident that the values got by Raoult's method are not the integral or so-called molecular weights of the solid species themselves, or what we have designated *mineral species*, but of the *chemical species* which result from the depolymerisation of these, and which pass into solution. These values, moreover, bear no obvious relations to the specific gravities of these solid species, as appears when we compare sugars like xylose, dextrose, saccharose and raffinose with each other, and with the dextrines and soluble starch; bodies which with

such widely different integral weights in solution have almost identical specific gravities in the solid state. It is, in the language of the atomistic school, "the molecular mass" of the dissolved substance which we determine by Raoult's method, and not that of the solid or liquid mineral species, from the depolymerisation of which, in the process of solution, is derived the chemical species; the molecular or, in other words, the integral weight of which ($H=1$) may vary widely in bodies nearly allied, as in hydrocarbons of identical centesimal constitution, different sugars, and certain amyloid substances. The total mineral condensation in such cases being essentially the same, the question is whether the depolymerisation or homogeneous disintegration which takes place in vaporisation or in solution shall resolve the mineral species into a greater or less number of chemical species.

Chemical species probably never assume liquid or solid forms. They are either vapors or gases, which by intrinsic condensation (polymerisation) pass into liquids or solids, or else, if their integral weight is too great to permit their existence in a gaseous condition at ordinary temperatures, unite with water, forming liquid hydrates, from which they separate, after a longer or shorter time, in solid or, more rarely, in liquid hydrated or anhydrous species. The appearance of such solid or liquid bodies in the midst of an aqueous solution marks the passage of the dissolved *chemical species* by polymerisation into a *mineral species*; a process often favored by mechanical agencies or by change of temperature.

§13. The significance of these relations is made more apparent by the writer's theory of solution, according to which there are formed in the process of aqueous solution definite compounds of the dissolved matters with water, accompanied with all the phenomena of chemical union; the further addition of water thereto giving rise either to new chemical arrangements of the substances present, or to simple admixtures of one definite solution or liquid species with another of unlike density. Examples of such admixtures of aqueous solutions are seen in the case of phenol and water, which when heated mix in all proportions, but on cooling separate into two layers, the lower a solution of phenol in water, and the upper a solution of water in phenol. Aniline and many other bodies present similar reactions with water below 100°C. , and like results are got through the agency of pressure at still higher temperatures. Thus salicylic acid heated with water in a

sealed tube above 100° gives a solution which separates suddenly, on cooling to 91° , into two layers, each of which, according to Alexéeff,¹ grows turbid independently as cooling goes on. Similar separations of liquids have been noticed by Hannay and Hogarth in the case of alcoholic solutions of calcic chloride and ferric chloride, under pressure. Moreover, the spontaneous separation, long suspected, of many saline solutions into layers of unlike density through the influence of gravity, has been confirmed by the studies of Bodländer and the more recent ones of Traube and Neuberg. The conversion of denser solutions into solid hydrous species is in many cases but a question of temperature. Liquidity is only an accident of solution. Not only is all solution chemical union, but "all chemical union is nothing else than solution. The resulting species are, as it were, dissolved in each other, for solution is mutual." All precipitation and all crystallisation from solution thus involve chemical change, and all chemical species may theoretically exist in soluble states, from which they pass into polymeric mineral species, often insoluble.²

§14. A given chemical species, whether elementary or complex in constitution, may in some cases pass through two or more higher *chemical forms*, by successive condensations, until at last it assumes a *mineral form* as a liquid or a solid species, which in the latter case may either be colloidal or may take on a crystalline shape; the whole process, from the simplest chemical form, constituting an ascending series, in which the older and simpler forms are not lost but latent. It is to the converse of this process, or, in other words, to the depolymerisation by solution of solid mineral forms, that reference was had when, in 1853, the writer insisted upon "those chemical changes which commence only with the destruction of crystalline individuality," as quoted above in §4; or, in other words, to the breaking up of *mineral species* by solution into *chemical species*.

§15. The mineral form itself is, however, in many cases subject to other changes, since the solid species may undergo alterations in density, in hardness, in fusibility and in crystalline shape with-

¹ Bull. Soc. chim. II, 38, 145.

² These views, set forth in 1853, and more fully in 1855, in *Thoughts on Solution and the Chemical Process*: Am. J. Sci. (11) 19, 100-103, and *Chemical Gazette* for 1855, p. 92, are reinforced in the *New Basis for Chemistry*, pp. 98-99, and in *The Theory of Solution*: Brit. Assoc. Adv. Science, Sec. B, 1888; *Chem. News* 58, 151. See also *Mineral Physiology*, etc., pp. 167-169. Similar views have since 1886 been put forward by Mendeléeff.

out passing by a process of fusion or solution. Thus, for example, of the many allotropic phases of solid sulphur we may designate three as the plastic amorphous or colloidal, the clinorhombic and the orthorhombic. Of these, the first two pass spontaneously after a time into the denser and more stable orthorhombic state, an alteration which, as Spring has shown, is accelerated by pressure. A still more striking case is found in tin, the gray brittle form of which, with a density of 5.8, by gentle heat, concussion or momentary pressure passes into the white malleable species with the density 7.3, and may again by considerable reduction of temperature revert to the lighter brittle species. So the orthorhombic calcium carbonate, aragonite, is, at a low red heat, transformed into the lighter rhombohedral form, calcite. Ice, moreover, at 0° passes by pressure into liquid water, with a considerable increase of density (as in the case of tin); the transformations of the two species being readily repeated by slight variations of temperature or of pressure. It would be easy to multiply instances of such changes of mineral form.

§16. In the case of insoluble non-volatile solids like tin and calcium carbonate we are precluded from the use alike of the vapor-density and the cryoscopic method as means of fixing the integral weight of the chemical species which by its polymerisation gives rise to the mineral species in question. We may add that even were the conditions such as to permit the application of either of these methods the presence of possible admixtures of different polymers might give rise to difficulties in their application, especially in cases where it is known that such polymers may have been simultaneously formed. Thus, for example, among the many polymers generated by the intrinsic condensation of acetylene, three, namely retene $(C_2H_2)_9$, cinnamene $(C_2H_2)_4$,—or rather its solid allotrope, metacinnamene—and benzene $(C_2H_2)_3$, are all solids at temperatures above 0° . An admixture of two or more of these might well have a fusing point which would tend to confound it with some intermediate species. Again, among the higher olefines, $(CH_2)_n$, three of which have been mentioned above (§8), octodecylene ($n = 18$), melts at 18° and has a density of 0.79; cerotene ($n = 27$) melts at 58° and has a density of 0.86; while melene ($n = 30$) melts at 62° and has a density of 0.89. Mixtures of any two of these would give rise to uncertainties like those which we have imagined in the case of the solid polymers

of acetylene. In both of these examples, it is true, separation of the intermingled hydrocarbons might be effected by differences in the solubility and the volatility of the polymeric species; but in other cases, where we have to deal with bodies alike non-volatile and insoluble, the problem becomes far more difficult. It is evident that, while in the case of gases and vapors the density varies directly as the integral weight of the chemical species, no such rule holds good in solids and liquids. This is well illustrated in the case of the three solid olefines just named, having, with small variations of density, integral weights for the chemical species which are to each other as 18 : 27 : 30, and also in that of the glucosic, diglucosic and triglucosic sugars, having for the chemical species integral weights nearly as 1 : 2 : 3, yet with specific gravities for the solid or mineral species which are almost identical.

§17. Among native mineral species there are not wanting instances of such mixtures, a good example being seen in the disulphide of iron, which constitutes alike the orthorhombic species marcasite, and the isometric species pyrite. Multiplied observations of specimens of the latter species by various skilled naturalists show that its specific gravity may vary from 4.80 to 5.00 and even 5.15 and 5.20 for well-defined pyritohedral crystals. On the other hand, marcasite itself may vary in specific gravity from 4.75 to about 5.00 (4.987), with a hardness on the scale of Mohs of 6.0-6.5; while the denser isometric species attains 6.5-7.0. The latter strikes fire strongly with steel, giving a faint sulphurous odor; marcasite, on the contrary, feebly, giving a strong odor. Differences in color and texture also distinguish the denser from the lighter sulphide. A. A. Julien, who has lately examined this question with great care, concludes that we have in these minerals of intermediate density an intermingling of two disulphides of unlike degrees of condensation. Each of these species would thus be dimorphous and might include admixtures of the other.¹ It is difficult to conceive any other explanation of these facts, which are precisely what we should expect in the case of admixtures of polymeric bodies like the hydrocarbons noted above. It will be found that an admixture of three parts of a disulphide of iron, sp. gr. 5.18, and two parts of one of sp. gr. 4.75, would give a mean sp. gr. of 5.00, which is that assigned by many

¹A. A. Julien, N. Y. Acad. Sci. 1886, 1887, Vol. 3, No. 12, 4, Nos. 3, 5, 6, 7.

observers to pyrite, and very near the maximum specific gravity of marcasite.

Similar differences in density are met with among the orthorhombic and isometric arsenides of cobalt, nickel and iron, represented by the general formula $MAAs_2$, as shown in safflorite and smaltite, verified by the recent studies of MacCay. Another example of the kind, uncomplicated by the question of dimorphism, is seen in sodium chloride. Several careful observers concur in giving for specimens of this substance at ordinary temperatures a sp. gr. of about 2.25 (2.20, 2.23, 2.26); and others, apparently equally worthy of confidence, have found about 2.00 (2.01, 2.03, 2.06, 2.08), while the greater number of observations range from 2.14 to 2.20. These wide variations in density in such a familiar species are the more remarkable for the reason that the chlorides of potassium and ammonium present no such notable variations. A similar condition of things is apparent in crystals of zircon, and many other cases might be cited showing that we have, as in the case of the iron disulphides, variable admixtures of two mineral species with the same centesimal composition but of unlike condensation.

§18. It will now be apparent that we have to deal with processes of condensation belonging alike to chemical species and to mineral species. Thus, for example, with acetylene, pentine and their polymers, we have in each case chemical species having a common centesimal composition with widely different co-efficients of chemical condensation, as is apparent when we compare their vapor-densities; which, moreover, present no simple or apparent relations to their specific gravities in the liquid or solid state. We may recall in this connection the already cited case of formaldehyde, of which the equivalent weight is fixed by its vapor-density as well as by Raoult's method, with those of xylose, glucose and the related sugars and amyloid bodies; species for which the chemical condensation presents a very wide range. In these cases we are enabled by vapor-density, by the cryoscopic method, or else by direct chemical analysis, to determine the minimum value of the chemical integer, and in this latter way we are led to assign in many cases very elevated numbers, as seen in such compounds as the cobalt amine salts and the polytungstates, the simplest admissible formulas of which give integral weights of thousands or tens of thousands.

§19. The history of the development of this modern conception in chemistry is one of such importance as to demand a somewhat extended study. The earliest statement, so far as the writer is aware, of the application of the doctrine of complex formulas, of high equivalent weights, and of homologous relations (already recognised among hydrocarbonaceous bodies in the domain of organic chemistry), to mineral, or inorganic, chemistry will be found in a paper by him in 1853. Therein it was contended that isomorphous solid species, at least, "have the same equivalent volume, so that their equivalent weights (as in the case of vapors) are directly as their densities; and the equivalents of mineral species are as much more elevated than those of the carbon series as their specific gravities are higher." Referring to the latter, "the hydrocarbonaceous, or so-called organic, species," and to the law of progressive or homologous series therein first pointed out by James Schiel, of St. Louis, and soon after adopted by Charles Gerhardt, it was said that "it may be expected that mineral species will exhibit the same general relations as those of the carbon series, and the principle of homology be greatly extended in its application. The history of mineral species affords many instances of isomorphous silicates, whose formulas differ by $n(\text{O}_2\text{M}_2)$, as the tourmalines, and the silicates of alumina and of magnesia."

It was then further declared that the native mineral carbonates or carbon-spars must be represented as polycarbonates having not less than from "twelve to eighteen equivalents of base replaceable so as to give rise to a great number of species"; among which the relations of their densities were said to "indicate the existence of several homologous genera which are isomorphous." In subsequent papers, in 1853 and 1854, attempts were made to show that in these polycarbonates, $n(\text{CMO}_2)$, the different values of n might be not less than 22, 25, 30, 36 and 40. Similar elevated formulas were also given in 1853 for various polysilicates, as in the cases of augite, amphibole and wollastonite, and of the feldspars, albite, anorthite and orthoclase. In this connection the complex silicates containing chlorides, carbonates and sulphates were considered and compared to basic salts.¹

¹ "Theory of Chemical Changes and Equivalent Volumes," *Am. J. Sci.* **15**, 226-234; *Phil. Mag.* (4), **5**, 526, and in a German translation in the *Chem. Centralblatt* of Leipzig for the same year (p. 849); also in the author's "Chem. and Geol. Essays," pp. 427-437. Further, "The Constitution and Equivalent Volume of Mineral Species," *Am. J. Sci.* **16**, 203-218, and,

The variations in the ratios of silica and alumina in nearly related species, and the apparent partial replacement therein of silica by the latter, then imperfectly understood, were noted in 1854 as seeming to invalidate the distinction between silica, as the negative or acidic member, and the positive or basylous member of these oxidised compounds, in which alumina was at that time still included.

§20. These views of polymerism in mineral species, involving on the one hand the conception of many equivalents of replaceable base, and on the other of many equivalents of the acidic or negative element, which might be either carbonic, silicic or boric oxide, or might include with the latter alumina, sulphates, carbonates or fluorides, though thus enunciated in 1853, found no favor among chemists until 1860, when Adolphe Wurtz again put forth the notion of polysilicates, citing in connection therewith the metastannates of Frémy, in which the negative element consists of 5(SnO_2). The similar metatungstates or tetratungstates, the pyroborates, the polyphosphates of Fleitmann and Henneberg, including tetraphosphates and dekaphosphates, and the not less complex phosphates of Wallroth, with 9(P_2O_5), soon showed that such a polymerism is not exceptional in negative or acidic oxides. The studies of other chemists, moreover, made it known that similar compounds, including different negative oxides of the same or of unlike valencies, were not less frequent; as appears in the complex phosphovanadates and arsenovanadates, in the aluminomolybdates, the ferrimolybdates, the borotungstates, the silicotungstates, the phosphotungstates, the phosphomolybdates, the stannophosphomolybdates, and salts of still greater complexity and of very high equivalent; often presenting series which illustrate in a striking manner the extension to such mineral species of the law of progressive series.

The high integral weight, the limited basicity and the partial instability of these complex salts are well illustrated in the phosphomolybdate of ammonia formed in the ordinary method for determining phosphorus thereby. This insoluble compound, when precipitated in presence of an excess of chlorhydric or nitric acid,

in abstract, in the author's "*Chem. and Geol. Essays*," p. 438, etc. Also, "*Illustrations of Chemical Homology*," *Proc. Am. Asso. Adv. Sci.* 1854, pp. 237-247; also, in abstract, *Am. J. Sci.* for September of the same year; and noticed, with extracts, in the author's "*Chem. and Geol. Essays*," p. 438 et seq. The whole question is further discussed in the author's "*Mineral Physiology, etc.*," pp. 283-295.

contains $12\text{MoO}_3 \cdot \text{PO}_4 \cdot (\text{NH}_4)_3$, besides $2\text{NO}_3 \cdot \text{H}_2\text{O}$ or $2\text{HCl} \cdot \text{H}_2\text{O}$, constituting a nitro-, or a chlorhydro-, phosphododekamolybdate; but by desiccation at 150° these volatile acids and water are expelled, leaving the phosphomolybdate with 3.78 per cent. of phosphoric oxide, P_2O_5 .

§21. We have thus endeavored to trace the steps by which, from the writer's first enunciation, in 1853, of complex formulas, high integral weights, and homologous, or progressive, series in mineral species, chemists have been led up to the comprehensive generalisation which Wolcott Gibbs has embodied in the important conception of what he has called complex inorganic acids. The results of chemical analysis, while they permit us in many instances to assign small integral weights to chemical species, force us to conclude that in other instances these integral weights are very elevated, conclusions which in the one and in the other case are confirmed alike by the vapor-density and by the cryoscopic method; which latter it will be desirable to verify still further by the study of many soluble salts of apparently complex constitution.

§22. The cases which we have just considered show in chemical species of related centesimal composition, as in formaldehyde, xylose, glucose, the higher sugars, the dextrines and soluble starch, integral weights rising from 30, 150 and 180 to numbers which cannot be less than thousands. These figures suggest for chemical species a range of integral weights which may conceivably rise to that of the mineral species itself. Instead of being, as in glucose and other sugars, a multiple of the chemical integer by a high number, the co-efficient for the mineral species becomes a small one, as in the case of the dextrines and soluble starch, or of the cobaltamines and the polytungstates. So far as is yet known, however, there intervenes, in all cases, a greater or less polymerisation, the study of which will be found to have important thermo-chemical relations.

If we consider the four groups of sugars represented chemically by xylose and arabinose (C_5), glucose (C_6), saccharose (C_{12}), and raffinose (C_{18}), but having for the mineral species essentially the same specific gravity, assumed to be 1.5, we shall have for the co-efficients of the mineral species, respectively, the numbers 214, 180, 94 and 54, corresponding to a common integral weight therefor of 32,100; xylose being $214(\text{C}_5\text{H}_{10}\text{O}_5)$, glucose $180(\text{C}_6\text{H}_{12}\text{O}_6)$, etc. In the case of the volatile polymeric hydrocarbons already

mentioned (§8), octodecylene $(\text{CH}_2)_{18}$, cerotene $(\text{CH}_2)_{27}$, and melene $(\text{CH}_2)_{30}$, assuming the specific gravities assigned for the solids, namely 0.79, 0.86 and 0.89, to be correct, we have respectively the co-efficients for the solid mineral species of 67, 48 and 45. Melene will be $45(\text{CH}_2)_{30}$, cerotene $48(\text{CH}_2)_{27}$, and octodecylene $67(\text{CH}_2)_{18}$.

§23. The ammonio-cobalt salts, from the results of chemical analysis, have necessarily high integral weights for the chemical species, and have assigned to them densities of about 1.7–1.8; the former figure corresponding to an integral weight for the mineral species of about 36,380.¹ The minimum chemical weight for the orthometaphosphate of luteocobalt ($=2540$) would demand a co-efficient for the mineral species of 14, since $14 \times 2540 = 35,580$. In like manner the soluble crystalline hydrous polyphosphotungstates have for sodium salts, according to Scheibler, specific gravities of 3.84–3.98, and for a barium salt 4.3. I find no determination of specific gravity for the highly complex polyphosphovanadate (§1) to which Gibbs assigns a chemical weight of 20,058, and which, should its co-efficient of polymerisation be 4, would have a specific gravity of 3.75, nearly. More or less uncertainty must, however, still exist with regard to the true chemical formulas, and consequently to the integral weights of chemical species of such complex constitution as those now under consideration. Under the name of tungsten-bronzes have been conveniently included several anhydrous crystalline bodies, metallic in luster, conductors of electricity and highly electro-negative, which are nevertheless oxidised compounds of tungsten and an alkali-metal. The tungsten-bronze first described by Wöhler is, in the opinion of Gibbs, probably $16\text{WO}_3.4\text{WO}_3.7\text{Na}_2\text{O} (=5002)$. To this has been assigned a specific gravity of 6.617; to another sodium species, 7.28; and to a potassium species, 7.60.

§24. The fact that in the soluble hydrous polytungstates, hydrocarbon radicles like methyl, ethyl and phenyl, may enter, helps to break down the barrier, not yet wholly removed, which once separated the so-called organic and inorganic compounds (§2). Even the stability of insoluble silicates is not proof against similar changes,

¹ The revision by Crafts in 1888 of Regnault's determination of the weight of a liter of hydrogen in the latitude of Paris, making it 0.08988 gram (instead of 0.08975 gram) gives—if $\text{O} = 15.96$ —for the integral weight of water 21,335 in place of 21,406. In the uncertainty which still prevails as to the precise value of oxygen as compared with hydrogen, we may yet retain for water—the unit of specific gravity for liquids and solids—the number hitherto adopted, 21,400, as a close approximation, since the difference would only involve an error of about three-thousandths of a unit in such specific gravities.

as shown in the case of artificial ultramarine. This, which is got as a blue, green or violet crystalline powder, appears to be essentially a peculiar sodium aluminosilicate in which the oxygen is partially replaced by sulphur. By digestion with a solution of silver nitrate a yellow substance is got in which silver replaces sodium, and this with ethyl iodide yields a compound into which the alcohol radicle enters, and which by subsequent treatment with sodium chloride gives off ethyl chloride and regenerates blue ultramarine. The silver in the yellow species may also be replaced by potassium or by lithium, the last giving also a blue ultramarine. Similar compounds are obtained from ultramarine with the iodides of amyl, allyl, and benzyl.¹ It is probable that only their great insolubility prevents us from getting somewhat similar results with more highly condensed silicates, such as the feldspars, micas and tourmalines.

§25. It will be clear to those who have followed the preceding argument, that in cases where neither the vapor-density nor the cryoscopic method can be invoked, that is to say in non-volatile and insoluble mineral species, we have not the means of determining the integral weight of the chemical species which by its subsequent condensation generates such mineral species; or of discovering whether this may have attained that condensation by a single step or by successive stages. Thus, by hypothesis, a solid like retene might be generated directly by the intrinsic condensation of acetylene, or from benzene; the production of the latter hydrocarbon marking an intermediate stage in the progress of homogeneous integration. What stages, if any, intervene in the passage from the soluble normal calcium carbonate to the insoluble crystalline mineral species, calcite and aragonite, we may never know, though from the existence of these two mineral species of identical centesimal composition with different degrees of condensation and of solubility in acids, corresponding to the differences observed in the various polymers of many hydrocarbons, aldehydes, etc., we may with great probability suspect the existence of intermediate and unstable stages of condensation in calcium carbonate. The same argument applies equally to the unlike forms of silicon dioxide, tridymite and quartz, differing alike in specific gravity and in solubility; to the two forms of iron disulphide; and to other cases too many to recall.

¹ For a summary of the results of the study of ultramarine by Neumann, Philipp and de Forcrand, see Watts, Dict. Chem., 3d. Suppl., 2069-2071.

§26. We can in very many cases recognise at least two distinct stages of polymerisation in the passage of a given chemical species, either simple or compound, into a mineral species. The first stage is seen when the vapor of sulphur (S_2) passes by intrinsic condensation into the denser vapor (S_8); gaseous acetylene into the vapor of benzene, of cinnamene, or of retene; or when formaldehyde dissolved in water is changed to an aqueous solution of formose. The second stage is seen in the passage of the dense sulphur vapor, the polymerised hydrocarbon vapors, or the dissolved formose, into liquid or solid forms. For the great multitude of mineral species of which the corresponding volatile or soluble species are unknown to us, the means of marking these separate stages are wanting, and we have but two data: the specific gravity of the mineral species, water being unity, and the equivalent weight as deduced from the results of chemical analysis; d = the specific gravity and p = the equivalent weight. The latter, for compound species, may be calculated from the simplest formula which represents intelligibly the results of such analysis, or—as we have elsewhere proposed as the basis of a wider comparison which should include all metallic oxides, salts and haloid compounds—by the adoption for p of a still simpler and an arbitrary unit. For all such species “we assume as the unit for p a weight including that of $H = 1$, of $Cl = 35.5$, or of $O \div 2 = 8$. By thus adopting a combining weight of 8.0 for oxygen, we get a unit which gives a common term of comparison for oxides, sulphides, chlorides, fluorides, and for intermediate compounds like the oxysulphides and oxyfluorides common in native species.” For all silicates, carbonates, sulphates, phosphates, and more complex species, we find the value for p “by dividing in all cases the empirical equivalent weight by twice the number of oxygen portions ($O = 16$) plus the number of chlorine or fluorine portions.”¹ This method was already adopted by the author in 1886, and he has since proposed to complete it by the device of a notation as near as may be monadic, in which, by the use of various kinds of type, the valencies of the combining elements are made apparent.²

¹ For a further discussion of this question see the author on Chemical Integration in *Am. J. Sci.* for August, and in *Chem. News* 56, 136, 142; also his volume, “A New Basis for Chemistry,” 1888, 2d ed., pp. 225-227, and a French translation thereof by Prof. W. Spring, with additions by the author, entitled “Un Système Chimique Nouveau,” Paris, 1889.

² See in the author’s “Mineral Physiology and Physiography” an essay on A Natural System of Mineralogy, with a Classification of Silicates; and later, Notes on Valency, Basicity, Complex Acids and Chemical Notation: *Chem. News* 61, 267.

§27. Since the arbitrary mean chemical unit p , thus assumed, represents in all cases an aliquot part of the chemical species, however simple or however complex, which by its final intrinsic condensation has generated the mineral species whose specific gravity ($=d$) is known, it follows that the equation $p \div d = v$, giving in v the reciprocal of the co-efficient of condensation, permits a ready comparison of the relative condensation in mineral species, upon which, as we have elsewhere endeavored to show, the hardness and the chemical indifference of solids depend.

It will be remembered that p , which represents the equivalent weight of the chemical unit, corresponds in the last analysis to the specific gravity of that unit, presumed to be gaseous—hydrogen gas at standard temperature and pressure being unity ($H=1$)—while d represents the specific gravity of the liquid or solid mineral species, liquid water at its point of condensation at standard pressure being unity ($1=21,400$). The value deduced from this conventional p is readily adapted to any rational formula which may be admitted for the species in question. Thus quartz, represented as silicon dioxide, $SiO_2=60 \div 4=15=p$, and this being divided by 2.65, the specific gravity of quartz, we find $v=5.66$, which for SiO_2 gives $v=22.64$. We have then the proportion

$$22.64 : 21,400 :: 1 : 945.$$

In other words, if simple silicon dioxide passes directly into the mineral species quartz, the co-efficient of condensation is approximately 945 or perhaps 950(SiO_2). Should it be found, as is probable, that silicon dioxide in its soluble colloidal condition is a polymer of greater or less equivalent weight, represented by $(SiO_2)_{10}$ or by $(SiO_2)_{50}$, the above co-efficient therefor would be divided by these numbers; the total co-efficient of mineral condensation, comprising two or even more stages, being in each case the same. In the application of Raoult's method to colloidal silica, the reduction of the freezing point, according to Sabanéeff, was so slight that the values all came within the limits of errors of observation,¹ as would also appear to be the case with soluble starch.

To take another example, calcite, $CCaO_3=100 \div 6=16.66=p$. Dividing p by 2.73, as the specific gravity of calcite, we find $v=6.10$ nearly, which for $CCaO_3$ gives $v=36.6$,

$$36.6 : 21,400 :: 1 : 584.$$

¹Am. J. Sci. (III), 40, 87.

The condensation from CCaO_3 to calcite of specific gravity 2.73, is thus represented by $584(\text{CCaO}_3)$. Here, too, as in the case of silicon dioxide, it is probable that there exists an intermediate polymer, represented by a soluble form of carbonate of lime, long since noticed by the writer.¹

§28. These numbers thus arrived at for quartz and for calcite are, of course, but approximations, since the exact equivalent weights of oxygen and of silicon are still uncertain, and since, moreover, there are small variations in the specific gravity of the mineral species themselves, from which Breithaupt with much plausibility conjectured, in the case of calcite, the existence of several species, rhombohedral in form, with specific gravities ranging from 2.652 to 2.754. At the same time we must not overlook the calcium carbonate, aragonite, harder and less soluble in acids, with a specific gravity of 2.94, showing a higher intrinsic condensation than any calcite.

We have spoken of the views advanced in this paper as based on an hypothesis. It is, however, an hypothesis founded on a belief in the universality and the invariability of the law of volumes, and one which appears to be in complete harmony with the facts of chemistry so far observed. As one of the conclusions of a lifetime devoted to the study of certain chemical problems discussed more at length in the later editions of his *New Basis for Chemistry*, the writer now submits his paper to the judgment of philosophers.

NEW YORK, *September*, 1890.

¹ Recently-precipitated and still gelatinous calcium carbonate is soluble in water containing small quantities of calcium chloride or of magnesium sulphate, a liter at ordinary temperatures holding for many hours a gram or more of the dissolved carbonate, which, however, finally separates completely in transparent hydrated crystals, $\text{CCaO}_3 \cdot 5\text{H}_2\text{O}$. See the *History of Lime and Magnesia Salts*, *Am. J. Sci.* 1866, (2) 13, 58, 59; also *Mineral Physiology*, etc., p. 168.

REVIEWS AND REPORTS.

THE ELEMENTS OF CRYSTALLOGRAPHY FOR STUDENTS OF CHEMISTRY, PHYSICS AND MINERALOGY. By G. H. WILLIAMS, Ph. D. Pp. viii + 250, with 383 Figs. New York: Holt & Co., 1890.

A concise statement of the principles of crystallography has long been needed by the chemist who is interested in the study of the internal structure of the substances with which he is daily in contact. The logical treatment of crystallography by Dr. Groth, in his treatise so well known under its title "*Physikalische Krystallographie*" (Leipzig, 1885), has rendered it one of the most valuable aids to that branch of chemists engaged in the solution of the problem with relation to the arrangement of molecules in space and of the atoms in the molecule.

The author of the present volume, largely based upon that of Groth, has sought not only to introduce the beautiful logic of the German crystallographer to English-reading students, but he has also attempted to simplify the discussion of crystal forms so that it may be grasped by the busy chemist and the young college man, and at the same time prove of value to the mineralogist. The result of his labors is a book that contains all of the fundamental truths established by the study of crystals, so stated that they are easily understood. Beginning with the explanation of the differences between chemical molecules and crystal particles, the book carries the reader through the seven crystallographic systems, introduces him to crystal aggregates, describes to him the causes of the imperfections in crystals, and finally gives him about thirty pages of hints on the projection and construction of crystal figures. Throughout the entire volume emphasis is laid upon the fact that the crystal forms are functions of chemical composition, and symmetry is made the basis of the discussion of the crystal forms.

The author deserves the thanks not only of English-reading students for giving them the first clear English exposition of the science which is the subject of his work, but he deserves as well the thanks of French and German chemists and physicists for sifting from the ponderous volumes of the German crystallographers their essential portions and incorporating them in such a convenient form. The publishers, also, are to be congratulated on their success in accomplishing such a difficult undertaking as was the publication of this little volume with its many unusual symbols and crystallographic figures. The book should receive a hearty welcome from every chemist as well as from every mineralogist.

W. S. B.

HYDRAZOIC ACID.

Dr. Theodor Curtius, of Munich, has obtained a new gaseous compound of nitrogen and hydrogen, and has described its properties in an address made in the chemical section of the recent German Scientific Congress at Bremen. Neither this address nor any article by the author has yet reached us; from an article in *Nature* we abstract a brief preliminary notice.

The gas has the composition HN_3 , and Curtius gives it the constitution $\text{H}-\text{N}-\text{N}$, proving it to be the hydrogen compound

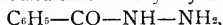


corresponding to the diazo-benzene-imide of Griess, $\text{C}_6\text{H}_5-\text{N}-\text{N}$.

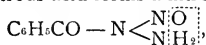


The gas dissolves in water with great avidity, forming a solution which possesses strongly acid properties, and dissolves many metals such as iron, copper and zinc, with evolution of hydrogen and formation of nitrides, the metal replacing the hydrogen. Curtius names this gas "Stickstoff-wasserstoffsäure." As English equivalent the name "Hydrazoic acid" is proposed.

In studying the properties of derivatives of hydrazine hydrate N_2H_4 , H_2O , Curtius found that benzoyl hydrazine,



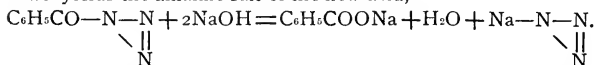
when treated with nitrous acid forms a nitroso compound,



which spontaneously changes, losing water, into benzoyl-azo-imide $\text{C}_6\text{H}_5-\text{CO}-\text{N}-\text{N}$; benzoyl-azo-imide saponified with



alkali yields the alkaline salt of the new acid,



On warming this sodium salt with dilute sulphuric acid, $\text{H}-\text{N}-\text{N}$



is liberated as a gas of fearfully penetrating odor, causing catarrh. Hot concentrated sulphuric acid decomposes the gaseous hydrazoic acid. The solution of the gaseous acid in water strongly resembles aqueous hydrochloric acid; on distillation a concentrated acid first passes over, and afterwards a more dilute acid of constant composition. The aqueous solution has the odor of the free gas and is strongly acid to litmus. With ammonia gas, hydrazoic acid gas forms dense white fumes of the ammonium salt N_4H_4 , or $\text{NH}_4-\text{N}-\text{N}$, a compound completely volatile below



100°, and crystallising, but not in forms of the regular system. The silver and mercurous salts are insoluble in water, the other salts are readily soluble. The barium salt, BaN_6 , crystallises from the solution in large brilliant anhydrous crystals. The silver salt, $\text{Ag}-\text{N}-\text{N}$, strongly resembles silver chloride, but



does not darken when exposed to light. It has fearfully explosive properties; one milligram of this salt, placed on an iron plate and touched with a heated glass rod, exploded with a loud detonation, distorting the plate. The mercurous salt is also explosive. The metallic salts are readily converted into ethereal salts when treated with haloid ethers. The phenyl salt thus prepared, $\text{C}_6\text{H}_5-\text{N}-\text{N}$, is in every way identical with the diazo-benzene-



imide of Griess.

E. RENOUF.

OBITUARY.

SILAS H. DOUGLAS died in Ann Arbor, Mich., August 26, 1890, at the age of seventy-four. He had been Professor of Chemistry in the University of Michigan from 1846 to 1877. The chemical laboratory of that institution, erected in 1856 and repeatedly extended, was the result of his labors, continued with energy through the active portion of his life. For a number of years his health had been infirm and he had remained in the retirement of his devoted family.

PROFESSOR HEINRICH WILL, the successor of Liebig at Giessen, died October 15, 1890. In the first rank among teachers of chemistry, he occupied a most enviable position. The many congratulatory letters received from all parts of the world on the occasion of the fiftieth anniversary of the date on which he received his degree, testify to the high reputation he had won for himself among chemists. Will is best known outside of Germany through his great work upon Chemical Analysis, and his editorship during many years of the *Jahresbericht*. He was a prominent figure in that distinguished group of the pupils of Liebig, of whom Kopp, Fresenius, v. Hofmann, and v. Pettenkofer still remain.



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